CH2M HILL
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June 24, 2014

Richard Ho
New Jersey Remediation Branch
USEPA Region II
290 Broadway, 19th Floor
NY, NY 10007-1866

Subject: Baseline Groundwater Sampling UFP-QAPP, Quanta Resources Corporation Superfund Site, OU1

Dear Mr. Ho:

On behalf of Honeywell, CH2M HILL has prepared work plan to complete a baseline groundwater sampling event at the Quanta Resources Corporation Superfund Site, Operable Unit 1 (OU1) prior to completion of a remedy in accordance with the Record of Decision (ROD).

This attached task specific Uniform Federal Policy – Quality Assurance Project Plan (UFP-QAPP) provides updates to the field tasks and field sampling plan (FSP) components of the work associated with this sampling event as required under the OU1 Remedial Design/Remedial Action Consent Decree (CD) for Civil Action Number 2:12-CV-7091-SRC-CLW. Data collection efforts will also be incorporated into the final design for the remedy under the Consent Decree being developed by EPA.

A total of 14 groundwater samples for analytical testing will be collected using low-flow sampling methods in accordance the original FSP (Parsons, 2005b) and as described in the 1998 "USEPA Region II Groundwater Sampling Procedure Low Stress (Low Flow) Purging and Sampling". Additional details are provided in Attachment A, UFP-QAPP. Groundwater samples will be collected from the monitoring wells as shown on Figure 1, samples will be analyze for the following:

- Dissolved metals using laboratory EPA Method 6010B
- Total volatile organic compounds (VOCs) using laboratory EPA Method 8260B
- Total semi-volatile organic compounds (SVOCs) using laboratory EPA Method 8270C

The individual analyses for groundwater are listed in Table 17-1 of the UFP-QAPP.

The results will be summarized within the Remedial Design Report and will provide a baseline for the Classification Exception Area (CEA).

If you have any questions in regards to the information provided herein, feel free to contact me at 267-250-7387 or Steve Coladonato, Honeywell Remediation Manager, at 302-791-6738.

Sincerely,

CH2M HILL

Stephen J. Zarlinski
Project Manager

WP-HCAA_GW Sampling
c: Steve Coladonato (Honeywell)
Erica Bergman (NJDEP)

Attachment A
Task-Specific UFP-QAPP

Draft

UFP–Quality Assurance Project Plan, Baseline Groundwater Sampling, Quanta Resources Corporation Superfund Site, OU1, Edgewater, New Jersey

Prepared for

Honeywell International Inc.

June 2014

CH2MHILL®

Document Control Number: CH2M-Quanta-BL-GW-v1

Prepared using 2012 EPA guidance (http://www2.epa.gov/fedfac/assuring-quality-federal-cleanups#ufp-qapp)

Contents

Acronyms and Abbreviations

%R	percent recovery
µg	microgram
BERA	baseline ecological risk assessments
bgs	below ground surface
CA	corrective action
CAR	corrective action request
CCV	continuing calibration verification
CEA	classification exception area
COC	chain-of-custody
CRQL	contract-required quantitation limit
DNAPL	dense nonaqueous phase liquid
DQI	data quality indicator
DQO	data quality objective
EB	equipment blank
EDD	electronic data deliverable
FD	field duplicate
FS	feasibility study
FTL	Field Team Leader
GC/MS	gas chromatograph/mass spectrometer
GW	groundwater
HCAA	high-concentration arsenic area
ICAL	initial calibration
ICV	initial calibration verification
ISS	in situ solidification/stabilization
kg	kilogram
L	liter
LCS	laboratory control sample
LCSD	laboratory control sample duplicate
MB	method blank
MDL	method detection limit
mg	milligram
mL	milliliter
MS/MSD	matrix spike/matrix spike duplicate
NAPL	nonaqueous phase liquid
NJDEP	New Jersey Department of Environmental Protection
NZ	NAPL zone
OU	Operable Unit
PARCCS	precision, accuracy, representativeness, comparability, completeness, and sensitivity
PC	project chemist
PCB	polychlorinated biphenyl

PDI	pre-design investigation
PDWP	predesign work plan
PID	photoionization detector
PM	Project Manager
PRP	potentially responsible party
QA	quality assurance
QAPP	quality assurance project plan
QC	quality control
QM	Quality Manager
RA	remedial action
RAC	remedial action contract
RAO	remedial action objective
RI	remediation investigation
RL	reporting limit
ROD	Record of Decision
RPD	relative percent difference
SI	supplemental investigation
SOP	standard operating procedure
SRB	subaqueous reactive barrier
SRI	supplemental remediation investigation
SRM	standard reference material
SVOC	semivolatile organic compound
TAL	target analyte list
TBD	to be determined
TOC	total organic carbon
TPH	total petroleum hydrocarbons
UFP-QAPP	Uniform Federal Policy for Quality Assurance Project Plans
USEPA	U.S. Environmental Protection Agency
VOA	volatile organic aromatic
VOC	volatile organic compound

TABLE1
CROSSWALK: UFP-QAPP WORKBOOK TO 2106-G-05 QAPP

Optimized UFP-QAPP Worksheets		2106-G-05 QAPP Guidance Section	
1 & 2	Title and Approval Page	2.2.1	Title, Version, and Approval/Sign-Off
3 & 5	Project Organization and QAPP Distribution	2.2.3	Distribution List
		2.2.4	Project Organization and Schedule
4 , 7 & 8	Personnel Qualifications and Sign-off Sheet	2.2.1	Title, Version, and Approval/Sign-Off
		2.2.7	Special Training Requirements and Certification
6	Communication Pathways	2.2.4	Project Organization and Schedule
9	Project Planning Session Summary	2.2.5	Project Background, Overview, and Intended Use of Data
10	Conceptual Site Model	2.2.5	Project Background, Overview, and Intended Use of Data
11	Project/Data Quality Objectives	2.2.6	Data/Project Quality Objectives and Measurement Performance Criteria
12	Measurement Performance Criteria	2.2.6	Data/Project Quality Objectives and Measurement Performance Criteria
13	Secondary Data Uses and Limitations	Chapter 3	QAPP Elements for Evaluating Existing Data
14 & 16	Project Tasks & Schedule	2.2.4	Project Organization and Schedule
15	Project Action Limits and Laboratory-Specific Detection / Quantitation Limits	2.2.6	Data/Project Quality Objectives and Measurement Performance Criteria
17	Sampling Design and Rationale	2.3.1	Sample Collection Procedure, Experimental Design, and Sampling Tasks
18	Sampling Locations and Methods	2.3.1	Sample Collection Procedure , Experimental Design, and Sampling Tasks
		2.3.2	Sampling Procedures and Requirements
19 & 30	Sample Containers, Preservation, and Hold Times	2.3.2	Sampling Procedures and Requirements
20	Field QC	2.3.5	Quality Control Requirements
21	Field SOPs	2.3.2	Sampling Procedures and Requirements
22	Field Equipment Calibration, Maintenance, Testing, and Inspection	2.3.6	Instrument/Equipment Testing, Calibration and Maintenance Requirements, Supplies and Consumables
23	Analytical SOPs	2.3.4	Analytical Methods Requirements and Task Description
24	Analytical Instrument Calibration	2.3.6	Instrument/Equipment Testing, Calibration and Maintenance Requirements, Supplies and Consumables
25	Analytical Instrument and Equipment Maintenance, Testing, and Inspection	2.3.6	Instrument/Equipment Testing, Calibration and Maintenance Requirements, Supplies and Consumables

TABLE1
CROSSWALK: UFP-QAPP WORKBOOK TO 2106-G-05 QAPP

Optimized UFP-QAPP Worksheets		2106-G-05 QAPP Guidance Section	
26 & 27	Sample Handling, Custody, and Disposal	2.3.3	Sample Handling, Custody Procedures, and Documentation
28	Analytical Quality Control and Corrective Action	2.3.5	Quality Control Requirements
29	Project Documents and Records	2.2.8	Documentation and Records Requirements
31, 32 & 33	Assessments and Corrective Action	2.4	ASSESSMENTS AND DATA REVIEW (CHECK)
		2.5.5	Reports to Management
34	Data Verification and Validation Inputs	2.5.1	Data Verification and Validation Targets and Methods
35	Data Verification Procedures	2.5.1	Data Verification and Validation Targets and Methods
36	Data Validation Procedures	2.5.1	Data Verification and Validation Targets and Methods
37	Data Usability Assessment	2.5.2	Quantitative and Qualitative Evaluations of Usability
		2.5.3	Potential Limitations on Data Interpretation
		2.5.4	Reconciliation with Project Requirements

QAPP Worksheets #1 and #2: Title and Approval Page

1. Project Identifying Information
   a. Site Name/Project Name: Quanta Resources Corporation Superfund Site, Operable Unit (OU) 1
   b. Site Location/Number: Edgewater, New Jersey
   c. Contract/Work Assignment Number: NJD000606442
2. Lead Organization
   a. Lead Organization Project Manager: Steve Zarlinski/CH2M HILL

      Signature: _____ Date: _____

   b. Lead Organization Quality Manager: Kyle Block/CH2M HILL

      Signature: _____ Date: _____

3. Federal Regulatory Agency: Richard Ho/USEPA Region 2 Remedial Project Officer

   Signature: _____ Date: _____

4. State Regulatory Agency: Erica Bergman/NJDEP, Project Manager

   Signature: _____ Date: _____

5. Other Stakeholders (as needed):

   Steve Coladonato/Honeywell International Inc., Site Remediation Manager

   Signature: _____ Date: _____

   Additional Personnel

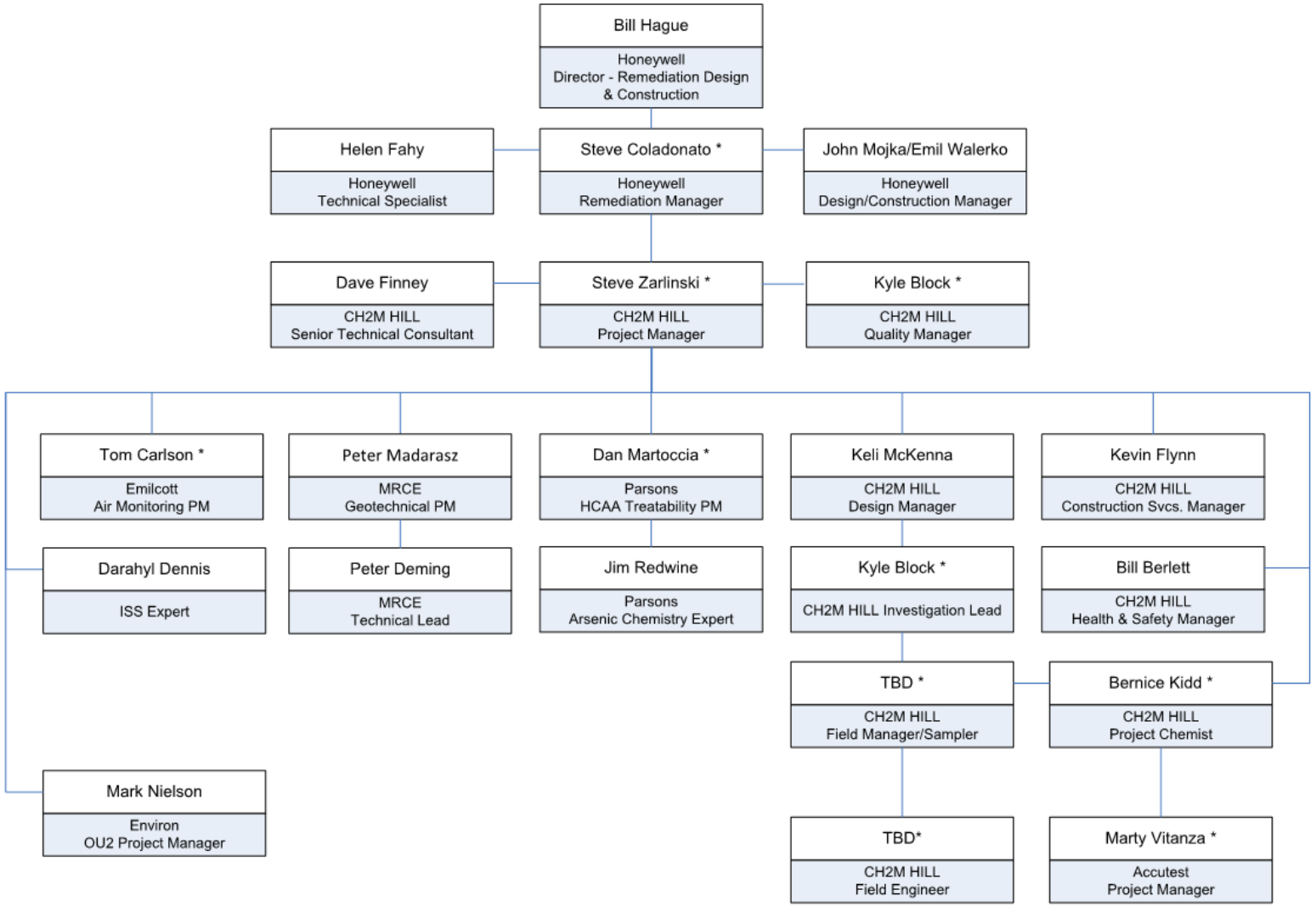
   Signature: _____ Date: _____

6. List plans and reports from previous investigations relevant to this project

Title	Approval Date
QAPP (Revised), Operable Unit 1, Quanta Resources OU1	October 2005
QAPP (Revised), Operable Unit 1, Quanta Resources OU1	November 2006
QAPP (Revised), Operable Unit 1, Quanta Resources OU1	July 2008
QAPP (Revised), Operable Unit 1, Quanta Resources OU1	October 2011
Quality Assurance Project Plan, Quanta Resources Corporation Superfund Site, Operable Unit 1, Edgewater, New Jersey	August 2012
Quality Assurance Project Plan, Quanta Resources Corporation Superfund Site, Operable Unit 1, Edgewater, New Jersey	August 2013

Title	Approval Date
UFP-Quality Assurance Project Plan for 2013/2014 Vapor Intrusion Sampling, Quanta Resources Corporation Superfund Site, OU1, Edgewater, New Jersey	September 2013
UFP-Quality Assurance Project Plan High Concentration Arsenic Area, Quanta Resources Corporation Superfund Site, OU1, Edgewater, New Jersey	March 2014

QAPP Worksheets #3 and #5: Project Organization and QAPP Distribution



* QAPP Recipient

Core Project Team Organization

Quanta Resources Corporation Superfund Site, OU1

CH2MHILL

QAPP Worksheets #4, #7, and #8: Personnel Qualifications and Sign-off Sheet

Name	Project Title/Role	Education/Experience	Specialized Training/Certifications	Signature/Date*
Organization: USEPA				
Richard Ho	Region 2 Remediation Project Manager			
Organization: NJDEP				
Erica Bergman	Remediation Project Manager			
Organization: Honeywell				
Steve Coladonato	Remediation Manager			
John Mojka/Emil Walerko	Design and Construction Manager			
Helen Fahy	Technical Specialist			
Organization: CH2M HILL				
Steve Zarlinski	CH2M HILL PM			
Kyle Block	Quality Manager			
Keli McKenna	Design Manager			
TBD	Field Manager/Field Sampler			
Bill Berlett	Health and Safety Manager			
Berney Kidd	Project Chemist			

*Signatures indicate personnel have read and agree to implement this QAPP as written.

This project will require uniquely trained personnel to perform specialized field reconnaissance, sampling, onsite/offsite analysis, data review, and other project functions. All project personnel are qualified and experienced in the project tasks for which they are responsible. All field personnel will have received the required OSHA 40-hour HAZWOPER certification and the annual 8-hour refresher course, if applicable. Training records/certificates will maintained by the CH2M HILL.

In addition to the aforementioned roles, subcontractors will be utilized on this project to complete the required work. The subcontractors will include analytical laboratories and field services subcontractors. The below table provides a list of current subcontractors and their contact phone numbers. Should this list change, an updated list will be provided to the personnel listed in Section 2.3 of this QAPP.

Subcontractor	Role	Contact Name	Telephone Number
Accutest	Analytical Laboratory	Marty Vitanza	(732) 329-0200

QAPP Worksheet #6: Communication Pathways

Communication pathways will follow the above organizational chart (Worksheet #3). The Honeywell RPM (Steve Coladonato) and the CH2M HILL PM (Stephen Zarlinski) will be the main contact for questions or concerns. Frequent and timely team communication is important and has a direct connection to the successful delivery of the remedial design. Individual tasks are listed in Worksheets #4, #7, and #8.

Communication Driver	Organization	Name	Contact Information	Procedure (Timing, Pathway, Documentation, Etc.)
Regulatory Agency Interface	EPA Region 2	Richard Ho	212-637-4372, Ho.Richard@epamail.epa.gov	Act as liaison between PRPs and United States government agency. Review and approve necessary documents associated with sampling and results. Provide written notice to proceed and approval of reports.
Regulatory Agency Interface	New Jersey Department of Environmental Protection	Erica Bergman	609-292-7406, Erica.Bergman@dep.state.nj.us	Act as liaison between PRPs and New Jersey agencies. Review and approve necessary documents associated with sampling and results. Provide written notice to proceed and approval of reports.
All project related tasks	Honeywell International Inc.	Steve Coladonato	302-791-6738, Steven.Coladonato@Honeywell.com	Act as liaison between CH2M HILL and USEPA. Provide review of all site documents.
All project related tasks	CH2M HILL	Steve Zarlinski	810-360-2061, Steve.Zarlinski@ch2m.com	
All project related tasks	CH2M HILL	Kyle Block	617-626-7013, Kyle.block@ch2m.com	Act as liaison between sample team and greater project team. Transmit necessary information to PM on status of sampling events and analytical updates.
QAPP changes prior to field work	CH2M HILL	Kyle Block	617-626-7013, Kyle.block@ch2m.com	Review QAPP during field mobilization and prep. Initiate corrective actions or changes associated with QAPP prior to mobilization.
QAPP changes during project execution	CH2M HILL	Field Manager	TBD	Field Sampler to identify corrective actions. Field Sampler initiates corrective action on identified field issues immediately or as defined during review.
Field correction actions	CH2M HILL	Field Manager, Steve Zarlinski	TBD/810-360-2061, Steve.Zarlinski@ch2m.com	PM and Field Sampler to identify corrective actions. Field Sampler initiates corrective action on identified field issues immediately or as defined during review.

Communication Driver	Organization	Name	Contact Information	Procedure (Timing, Pathway, Documentation, Etc.)
Site health and safety issues	CH2M HILL	Field Manager	TBD	Conduct Daily Health and Safety Meetings and make decisions regarding health and safety issues. Communicate with PM as appropriate.
Analytical actions/ reporting of data and release of data, facilitate data management, sample receipt	CH2M HILL	Berney Kidd	530-229-3203, Bernice.Kidd@CH2M.com	Provide electronic data, sample ID, locations and analysis. Transmit sample tracking information. Receive and review data packages before data is used. Initiate data validation of subcontractor laboratory data.
Analytical actions, laboratory-specific actions	Accutest	Marty Vitanza	732-329-0200, martyv@accutest.com	Communicate to PM as appropriate. Document situation and effect in a data quality report prepared as part of final report.

QAPP Worksheet #9: Project Planning Session Summary

Date of planning session: April 7, 2014

Location: Conference Call

Purpose: Baseline Groundwater Sampling Discussion

Participants:

Name	Organization	Title/Role	Phone/Email
Dave Finney	CH2M HILL	Senior Technical Consultant	617-626-7024, david.finney@ch2m.com
Kyle Block	CH2M HILL	Quality Manager	617-626-7013, Kyle.block@ch2m.com
Lynne Tseng	CH2M HILL	Engineer	650-353-8579, Lynne.tseng@yahoo.com

Agenda

1.) Next Steps
   a. Field test and sample collection
   b. Understand site wide locations
   c. Develop approach
   d. Identify additional data needs prior to OU1 remedy

2.) Review of Critical Items
   a. Obtain access with City Place to sample wells
   b. Short work plan for Item 2(a) for submittal
   c. Schedule

Action Summary	Notes	Responsible Party
Develop preliminary scope with figure showing locations	Work with rest of team to understand requirements of CEA and other portions of the site	Lynne Tseng
Prepare a work plan for submittal to EPA. This to include only the UFP-QAPP with a letter.	None	Kyle Block
Obtain access from various parties	Honeywell to provide email	Honeywell
Schedule sampling event	Planned for end of May pending approval from EPA on work plan	CH2M HILL

QAPP Worksheet #10: Conceptual Site Model

This QAPP addresses the baseline groundwater sampling event prior to implementation of the OU1 remedy. Other field activities will be addressed under separated QAPPs submitted in conjunction with relevant work plans. The following subsections present the conceptual site model for OU1.

Site Description

The Site is located at the intersection of River Road and Gorge Road in Edgewater, New Jersey. A vacant lot referred to as the Quanta property, portions of River Road and Gorge Road, and properties and portions of properties surrounding the Quanta property comprise the upland portion of the Site, or OU1. The area of OU1 is approximately 24 acres. The Site is adjacent to the Hudson River. Figure 1 depicts the properties constituting OU1.

The Quanta property contains the following:

- Exposed former tank and building foundations
- Remnants of a former oil-water separator
- A wooden bulkhead along the shoreline
- Remains of wooden docks

The property is generally flat and at a lower elevation than River Road to the west and the City Place property to the north. The Quanta, 115 River Road, and i.Park properties are all at a similar elevation, one corresponding to the land surface during industrial use (prior to 1982). River Road and City Place are located at higher elevations due to more recent placement of fill material.

Site History

The brief site history below was provided within the Record of Decision (ROD).

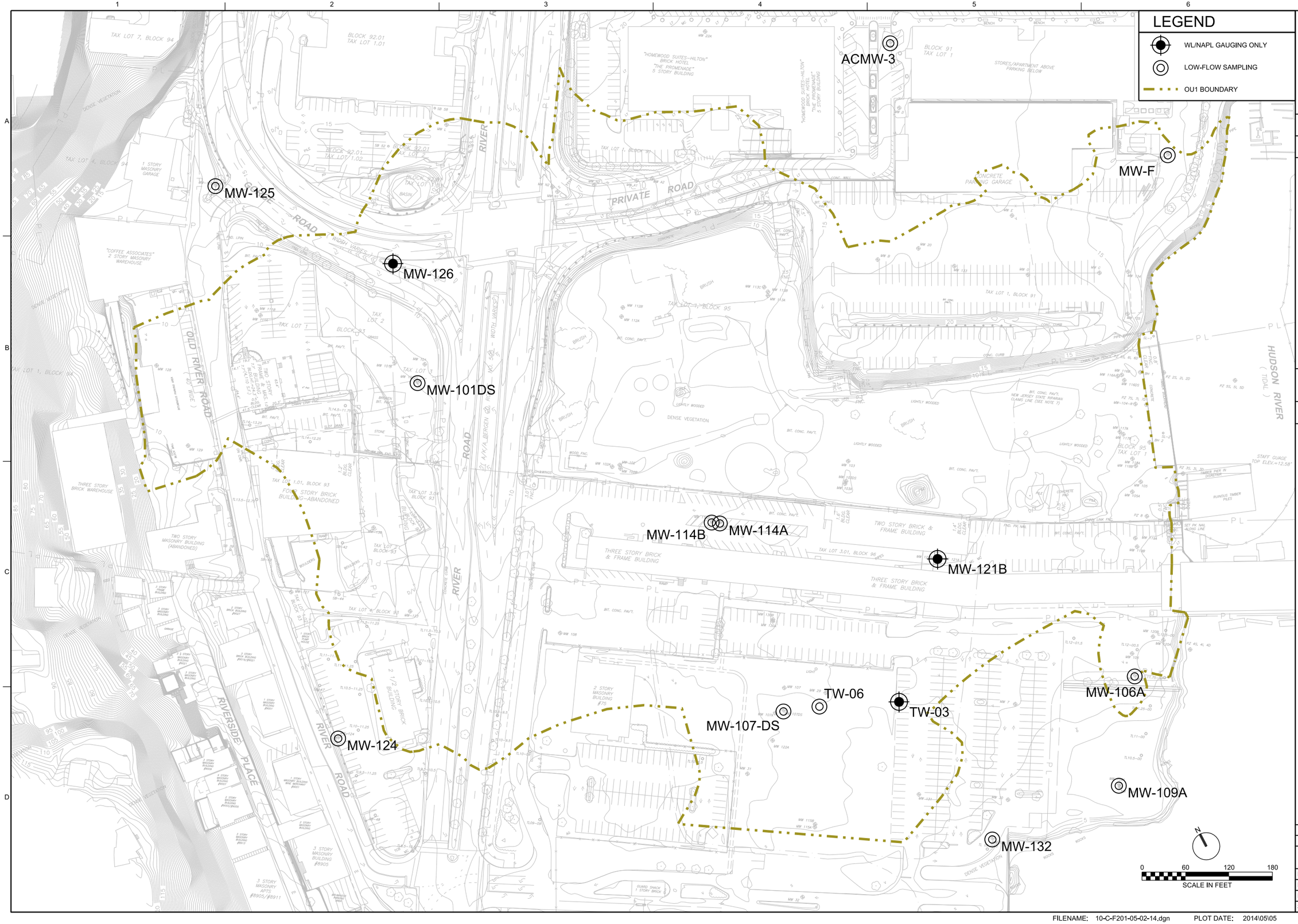
The Quanta site is located at River Road and the intersection of Gorge Road, Edgewater, New Jersey. At the center of the site is a 5.5-acre vacant lot, referred to as the Quanta property, surrounded by a number of developed and undeveloped parcels, portions of which are also considered part of the site. Sections of River and Gorge Roads have been constructed on top of the site. The land portion of the site is approximately 24 acres. The site also includes an area of sediment contamination in the Hudson River. The extent of the Hudson River sediments affected by the site will be determined as part of an ongoing Operable Unit 2 (OU2) Remedial Investigation and Feasibility Study (RI/FS) that is separate from this response action.

The site is characterized by contamination from a variety of industries that operated there from at least the 1870s to 1981. These industries included coal tar processing, chemical manufacturing, and waste oil storage. The 5.5-acre Quanta property is a remnant of an industrial coal tar facility that once covered approximately 15 acres.

Geology

At the upland portion of the Site, the overburden stratigraphy listed below is generally observed (in order encountered from ground surface):

Stratigraphic Unit	Description
Fill material	Up to 35 feet of fill material consisting of a mixture of gravel, sand, and silt with brick, wood, concrete fragments, coal, cinders, and slag.
Peat/clayey peat	Up to 25 feet of organic peat or meadow mat with varying amounts of clay, fine sand, and silt. The peat/clayey peat deposits are discontinuous and have been observed primarily in borings completed near River Road, Block 93, and the former Lever Brothers property.



NO.	DATE	REVISION	DR	CHK	APVD
DSGN	L TSENG	PA KARABAN			BY APVD

CH2MHILL®

HONEYWELL INTERNATIONAL INC.
QUANTA RESOURCES CORPORATION
SUPERFUND SITE
Edgewater, New Jersey

FIGURE 1
ARSENIC IN SHALLOW ZONE - OU1

VERIFY SCALE
BAR IS ONE INCH ON ORIGINAL DRAWING.
0 1"

DATE	
PROJ	428872
DWG	FIGURE 1
SHEET	of

FILENAME: 10-C-F201-05-02-14.dgn PLOT DATE: 2014\05\05 PLOT TIME: 7:57:24 AM

Stratigraphic Unit	Description
Soft organic silt	Up to 68 feet of soft gray-to-black organic silt containing wood, roots, and shell fragments. This unit is also included in the estuarine and salt marsh deposits. The soft organic silt is typically present only within 100 feet of the shoreline throughout the entire study area and represents former river sediments that were buried during shoreline filling. It pinches out to the west and against the bedrock high to the northwest on the former Celotex property. Moving east to west, the organic silts become the main layer within the Hudson River Basin, dipping downward extending to nearly the bedrock with a thin layer of till between the silts and bedrock.
Shallow native sand	Up to 21.5 feet of fine to medium/coarse sand with varying amounts of gravel and fines. In the central portions of the Quanta property and the northern portion of the former Lever Brothers property where the peat/clayey peat and soft organic silt are absent, the shallow native sand resides directly beneath the fill unit. South of the high bedrock elevations within the former Celotex property, native sands along the shoreline dip down, eventually pinching to an end along the shoreline of the Hudson River Basin and giving way to the soft organic silts.
Silty clay (confining unit)	Up to 35 feet of continuous silty clay with varying amounts of fine sand. The silty clay represents a lake-bottom unit that underlies the estuarine and salt marsh deposits. The silty clay serves as a confining unit and an aquitard between both the overlying native sand and fill units and the underlying deep sand deposits. It is found across most of the site with an undulating surface that dips eastward in close proximity to the existing shoreline and pinches out towards the north against a bedrock high at the former Celotex property. On the southern portion, the silty clay along the shoreline dips down in a manner similar to what is observed with the native sands, eventually pinching to an end along the shoreline of the Hudson River Basin and giving way to the soft organic silts.
Deep sand	Ranging up to approximately 32 feet of fine to coarse sand, sand with varying amounts of silt and clay, and silt and clay with varying amounts of sand. The deep sand represents a lacustrine fan unit that lies beneath the confining silty clay unit. Like the overlying silty clay confining unit, the deep sand dips eastward under the Hudson River and pinches out towards the north against the bedrock high present on the former Celotex property and to the west against the rising Palisades ridge. On the southern portion of the Site, the deep sands follow the bedrock surface and extend farther from the shoreline below the “estuarine and salt-marsh deposits” into the Hudson River Basin.
Till	Up to 12 feet of a very dense, low-permeability, reddish-brown to reddish-yellow silty sand and sand with gravel, cobbles, and boulders. Along the shoreline to the south of PZ-6D, and to a lesser extent to the north Moving from east to west into the Hudson River basin, the till deposits slope downward dramatically giving way to a thickening of the organic silt deposits.
Bedrock	The Stockton Formation composes the underlying bedrock formation at the site and is found at depths ranging from 8.5 feet (at the bedrock high in the south-central portion of the former Celotex property) to 86 feet below ground surface (bgs). Its appearance in core samples collected during the RI consisted of variably consolidated alternating sandstone and siltstone lenses with a variety of colors, including, red, white, pink, brown-gray, and brown-yellow. Towards the east and southeast bedrock dips dramatically forming the Hudson River channel.

Three distinct hydrostratigraphic units exist at the Site above the bedrock surface. The shallowest unit consists of an unconfined, surficial water-bearing zone extending from the water table—approximately 4 feet below ground surface (bgs)—to approximately 15 to 20 feet bgs. This unit is underlain by a silty clay aquitard approximately 10 to 20 feet thick. Last, a confined water-bearing “deep sand” unit between 5 and 20 feet thick exists between the aquitard (confining unit) and the surface of the bedrock (Stockton Formation). The shallow saturated zone and deep sand units are not hydraulically connected.

Shallow groundwater flowing eastward toward the Hudson River is largely diverted to flow north and south once it reaches the shoreline, as a result of the presence of a wooden bulkhead. However, much of the groundwater above the clay confining unit flows beneath the bulkhead in the organic silt and shallow sand. Groundwater discharges to surface water through the river sediments in areas of upwelling north of and adjacent to the wooden bulkhead and to a lesser degree offshore south of the bulkhead.

Source Areas

Soil and groundwater at OU1 contain constituents from industries that operated on various portions of the Site from at least the 1870s to 1981, including coal tar processing, chemical manufacturing, and waste oil storage. A substantial amount of data and information was collected and assessed during the OU1 RI and various supplemental investigations and has achieved the objective of completing a comprehensive site characterization of the Site. The RI and various supplemental investigations included the following:

- Characterization of OU1 sources
- Determination of the nature and extent of contamination
- Evaluation of fate and transport of constituents of interest
- Assessment of potential risks to human health and the environment

Soils at OU1 have been found to contain source material in the form of principal threat and low-level threat waste. Principal threat wastes are considered source materials, that is, materials that include or contain hazardous substances, pollutants or contaminants that act as a reservoir for migration of contamination to groundwater, surface water, or as a source for direct exposure. Principal threat wastes are those source materials considered to be highly toxic or highly mobile that generally cannot be reliably contained or would present a significant risk to human health or the environment should exposure occur.

NAPL

The location, nature, and extent of the NAPL at OU1 have been comprehensively delineated through the RI process for the purposes of remedial design and implementation. NAPL is found throughout the Site and is made up of aromatic volatile organic compounds (VOCs) and semivolatile organic compounds (SVOCs). Most of the SVOCs are polycyclic aromatic hydrocarbons. Coal tar materials found at the Site range from low-viscosity liquids to solid tar. NAPL at the Site is identified as either free-phase or residual NAPL. Free-phase NAPL is able to collect in monitoring wells, whereas residual NAPL is present in quantities insufficient to allow mobility. Most of the free-phase NAPL at the Site is denser than water and is present in six discrete areas (NAPL zones [NZs] 1 through 6), shown in Figure 1. These NZs were defined on the basis of one or more of following factors:

- Thickness of visually observed NAPL as well as TarGOST response indicating NAPL
- Lateral and vertical separation between areas where visual observations and TarGOST results indicated significant thicknesses of NAPL
- Observation of free-phase (i.e., mobile) NAPL in monitoring wells

All principal threat NAPL at the Site (i.e., the portion of the NAPL for which active remediation is required per the ROD) is present within the boundaries of these six zones (Figure 1). Exposure through direct contact, ingestion, or inhalation is plausible for NZ-1 and NZ-2, and the potential is likely that future use of the Site could result in exposure if appropriate remedial actions are not implemented. Direct exposure to NAPL in NZ-3, NZ-4, or NZ-6 is unlikely, even under a construction scenario, given their depth (generally deeper than 10 feet below ground surface). Without additional remedial effort, there is the potential for the migration of free-phase NAPL to sediment and surface water in the Hudson River from NZ-2 and NZ-5. As indicated in the ROD, release of free-phase NAPL from NZ-1, NZ-3, NZ-4, and NZ-6 to sediments is not plausible.

Outside the defined NAPL zones and throughout the Site, NAPL is present as residual NAPL or thin, discontinuous pockets of free-phase NAPL that have not been found to be contiguous with the defined NAPL zones. These areas contain constituents exceeding soil remediation values but are not identified as source areas, and therefore they "can generally be managed in place with engineering controls (capping) and proper land-use restrictions." (ROD)

High-Concentration Arsenic Area

The HCAA lies beneath a cover and fill material, and a portion is located beneath an active access ramp to the City Place development. The extent of the HCAA is defined as soil concentrations of arsenic greater than 1,000 milligrams per kilogram (mg/kg). The 1,000 mg/kg boundary (i.e., the HCAA) as depicted was developed using

historical data collected during the investigation, remediation, design, and development of the City Place property, and new data collected during the RI and supplemental investigations. The cover placed during construction of the City Place development extends beyond the delineated 1,000 mg/kg boundary along the edge of River Road on the Quanta property. The extent of the HCAA and the extent of the cover are depicted in Figure 1.

Arsenic Areas

Eight separate sources of soluble arsenic to groundwater and of other inorganic constituents in groundwater were identified as principal threat waste within the lateral extent of OU1 but outside the HCAA. Each arsenic area has elevated soil concentrations that have a potential direct-contact risk to human health defined as greater than 390 mg/kg for arsenic contamination in the shallow, unsaturated soils (approximately the first 4 feet of surface soil) and 1,000 mg/kg for deeper soils. The ROD refers to these areas as "shallow arsenic hotspots," although these areas may contain residual NAPL or overlap areas delineated as NAPL zones (Figure 1). One of these arsenic areas (referred to as AA-3), located on the i.Park property, was excavated in December 2010 by i.Park Edgewater, LLC, with oversight by CH2M HILL. The remaining seven arsenic source areas and the HCAA are depicted in Figure 1.

Site-wide Soil

Outside the areas defined as NAPL zones, residual NAPL, discontinuous pockets of free-phase NAPL, and site-related constituents are found in saturated and unsaturated soil. The primary site COCs driving the remediation are VOCs, SVOCs, and metals, particularly arsenic and lead. Remedial evaluations and design are being based on a subset of representative constituents:

- VOCs: benzene, ethylbenzene, toluene, and xylenes
- SVOCs: naphthalene and benzo(a)pyrene
- Arsenic
- Lead

Some of the remaining constituents detected less frequently above the soil remediation goals will be addressed in source areas through the remedial actions for the source areas. Outside the source areas, capping and institutional controls will meet the remedial action objectives for these other constituents by preventing direct contact.

Site-wide Groundwater

Similar Site-related constituents were detected in groundwater throughout the site. As noted in the ROD, "groundwater contamination above screening criteria, with similar constituents, has been identified from remedial investigations of all neighboring properties"; therefore, a complete delineation of the extent of groundwater impacts from the Site is not possible. EPA concluded that the factors listed below along with "the presence of off-site sources and regional characteristics…would undermine a successful restoration within OU1."

Type of Factor	Characteristics Limiting Groundwater Restoration Potential
Contaminant	Widespread presence of NAPL (primarily as DNAPL), and recalcitrant DNAPL-related constituents
	Long history of industrial use and associated releases at and outside of the site
	Volume and depth of contaminated media
	Presence of arsenic in soil and groundwater, and the collocation of arsenic and DNAPL
Hydrogeologic	Complex geology consisting of interbedded and undulating layers of sands, silts and clays with discontinuous peat deposits
	Heterogeneous soil conditions and the presence of low permeability materials such as silts and clays
Site setting	Highly urbanized environment with significant surficial and subsurface infrastructure

DNAPL, dense non-aqueous-phase liquid.

A waiver of groundwater Applicable or Relevant and Appropriate Requirements within the OU1 boundary was granted by EPA on the basis of technical impracticability from an engineering perspective, and Remedial Action Objectives (RAOs) were developed to prevent unacceptable exposure and limit offsite migration. The complete evaluation of groundwater restoration potential is documented in the technical impracticability evaluation (CH2M HILL, 2010).

Remedial Action Objectives

The ROD established RAOs for principal threat waste, soil, and groundwater. Remedial action objectives for principal threat wastes and other media at the Site are as follows:

Material	Remedial Action Objectives
Principal threat waste	Remove, treat, or contain principal threat waste, to the extent practicable.
	Prevent exposure to NAPL and arsenic source material that poses an unacceptable human health risk.
	Prevent current or potential future migration of free-phase NAPL to the Hudson River or to areas that would result in direct contact exposure.
	Mitigate free-phase NAPL that poses a potential source of vapor intrusion and resulting inhalation exposure within existing or potential future structures.
	Mitigate NAPL and arsenic principal threats as sources of groundwater contamination, to the extent practicable.
Soil	Prevent or minimize potential human exposure through direct contact, ingestion, dust inhalation, or vapor intrusion that presents unacceptable risk from exposure to contaminated soil attributable to the site.
	Prevent or minimize potential erosional transport off site or to the Hudson River of contaminated soils at concentrations posing unacceptable risk.
Groundwater	Prevent or minimize potential exposure by contact, ingestion, or inhalation/vapor intrusion that presents unacceptable risk from exposure to contaminated groundwater attributable to the site.
	Prevent migration and preferential flow of site contaminants in groundwater to sediments and surface water of the Hudson River at levels posing an unacceptable risk to human health or ecological receptors.

Selected Remedial Action

The Selected Remedy described within the ROD involves the solidification/stabilization of NAPL and arsenic source areas, capping and institutional controls, coupled with the installation of a groundwater containment remedy, a subaqueous reactive barrier in the Hudson River to mitigate contaminated groundwater releases. The components of the Selected Remedy include:

- On-site solidification/stabilization of an estimated 150,000 cubic yards of contaminated soil containing arsenic and NAPL, primarily by in-situ solidification/stabilization (ISS).
- Recoverable deep NAPL will be collected utilizing recovery wells or recovery trenches and NAPL collected and disposed of offsite.
- Installation of a vapor mitigation system and basement sealing at 115 River Road; construction of a temporary barrier wall at 115 River Road along the shoreline to isolate untreated free phase NAPL from the Hudson River and sediments.
- Capping of contaminated soils remaining on site at concentrations greater than the Remediation Goals for residential direct contact with a multilayer cap as approved by USEPA.
- Installation of a subaqueous reactive barrier (SRB) in Hudson River sediments, coordinated with a future OU2 remedy.

- Operation and maintenance for the active components of the remedy, such as the Deep NAPL collection system and vapor intrusion systems, monitoring of the site over the long term to assure the protectiveness of the Remedy, and institutional controls; implementation of a long-term sampling and analysis program to monitor the contamination at the site in order to assess groundwater migration, and the effectiveness of the remedy over time.

QAPP Worksheet #11: Project/Data Quality Objectives

This QAPP addresses a baseline groundwater sampling event prior to implementation of the OU1 remedy. The ROD (p. 100) requires "implementation of a long-term groundwater sampling and analysis program to monitor the nature and extent of groundwater contamination at the site, in order to confirm that the footprint of the site-related groundwater contamination is not increasing." Biennial groundwater monitoring is also a requirement to maintain the CEA. Monitoring wells to be included in the long-term groundwater monitoring plan will be selected so that the following design objectives and monitoring well selection criteria will be met:

- Quantity/distribution of monitoring wells is sufficient to satisfy biennial reporting requirements to maintain the CEA
- Quantity/distribution of monitoring wells is sufficient to monitor downgradient or at the leading edge of groundwater impacts outside of ISS areas and deep NAPL
- Quantity/distribution of monitoring wells is sufficient to monitor near shore conditions to support design of the subaqueous reactive barrier
- At least two wells are screened in the deep sand

Sentry wells for deep NAPL monitoring may be used for groundwater monitoring as long as NAPL is not present.

The purpose of this pre-remedy groundwater sampling event is to collect more recent groundwater sampling results to be compared to historical results, where available. Data will be used to develop the sitewide long-term groundwater monitoring plan during remedial design. Post-remediation groundwater data will be evaluated in context of these baseline results. Data for this event will be provided to USEPA and NJDEP for their review as part of the design process associated with the ROD.

The final list of monitoring wells to be included in long-term monitoring will be determined during remedial design, and may include additional monitoring wells or exclude one or more of the monitoring wells sampled as part of this event.

The project-specific detection limits for each sampled media are specified on Worksheet #15 for all parameters and media which are being analyzed. Data will meet the DQOs that have been specified for the site per Worksheets #12, 18, and 28.

The sampling design and rationale, including the location and reason for each individual sample is included within Worksheets #17 and #18 of this UFP QAPP. Worksheets #19, 20, 24–28, and 30 specify additional analysis design requirements.

Data collected as part of this scope will be archived in accordance with Worksheet #29. Data from the subcontracted laboratories will be received in electronic format and validated accordingly by CH2M HILL. Hard copies of the field data including the field logs will be archived in the project files.

QAPP Worksheet #12: Measurement Performance Criteria

As part of this sampling event, environmental samples will be collected for groundwater. The groundwater samples will be required to meet selected measurement performance criteria (MPC) as indicated in the below tables. The quality of the data to be collected for this project will be verified through appropriate MPCs established for both sampling procedures and analytical methods. These MPCs should be satisfied in order to support defensible decisions and provide sufficient data for ultimately completing the implementation of the remedial action.

The MPCs should relate to data quality indicators (DQIs), consisting of precision, accuracy, representativeness, comparability, completeness, and sensitivity, commonly referred to as precision, accuracy, representativeness, comparability, completeness, and sensitivity (PARCCS) parameters. The DQIs are defined as follows:

Precision

Precision is a measure of reproducibility of analytical results. It can be defined as the degree of mutual agreement among individual measurements obtained under similar conditions. Total precision is a function of the variability associated with both sampling and analysis. Precision will be evaluated as the relative percent difference (RPD) between field duplicate sample results and laboratory sample duplicates, or between the MS and MSD results. Field duplicates will compose 10 percent of the sampling effort. MS/MSD samples will be field designated at a 5 percent frequency.

Accuracy

Accuracy is the degree of agreement between a measured value and the “true” (or expected) value. It represents an estimate of total error from a single measurement, including either systematic error (bias) or random error that may reflect variability due to imprecision. Accuracy is evaluated in terms of percent recoveries determined from results of MS/MSD and laboratory control sample (LCS) analyses.

Representativeness

Representativeness is the degree to which sample data accurately reflect the characteristics of a population of samples. It is achieved through a well-designed sampling program and by using standardized sampling strategies and techniques, and analytical procedures. Factors that can affect representativeness include site homogeneity, sample homogeneity at a single point, and available information around which the sampling program is designed. Using multiple methods to measure an analyte can also result in nonrepresentativeness of sample data.

Comparability

Comparability addresses the degree to which different methods or data agree or can be represented as similar. Comparability is achieved by using standard methods for sampling and analysis, reporting data in standard units, normalizing results to standard conditions, and using standard and comprehensive reporting formats.

Completeness

Completeness is a measure of the amount of valid data collected using a measurement system. Completeness is expressed as a percentage of the number of measurements that are specified in the Work Plan.

Sensitivity

Sensitivity is the ability of a method or instrument to detect the target analytes at the level of interest. Sensitivity can be measured by calculating the percent recovery of the analytes at the quantitation limit, which is the minimum concentration of an analyte that can be routinely identified and quantified above the method detection limit by a laboratory.

Matrix: Water

Analytical group or method: Volatile organics, SW-846 8260B

Concentration level: Low

Data Quality Indicator (DQI)	QC Sample or Measurement Performance Activity	Measurement Performance Criteria
Precision	Field Duplicates	≤30% RPD for analytes at least 5X reporting limit
Accuracy/Precision (laboratory)	Laboratory Control Sample and Laboratory Control Sample Duplicate	Criteria listed in Table 28-1
Sensitivity	Initial calibration and Form I for all environmental samples	Reporting limit 1 µg/L or better for chlorinated VOCs
Accuracy	Internal Standards	Criteria listed in Table 28-1
Accuracy/Precision	Matrix Spike and Matrix Spike Duplicate	Criteria listed in Table 28-1
Accuracy	Surrogate Compounds	Criteria listed in Table 28-1
Accuracy	Lab Method Blank, Field (rinsate) blank, trip blank	< RL

Matrix: Water

Analytical group or method: Metals, SW-846 6010C and SW7470A for mercury

Concentration level: Low

Data Quality Indicator (DQI)	QC Sample or Measurement Performance Activity	Measurement Performance Criteria
Precision (field)	Field Duplicates	≤ 30% RPD for analytes at least 5X reporting limit
Precision (laboratory)	Laboratory Control Sample Duplicate and Matrix Spike Duplicate	Criteria listed in Table 28-4
Precision	Serial Dilution	Criteria listed in Table 28-4
Sensitivity	Initial calibration and Form I for all environmental samples	Reporting limit to meet or exceed USEPA CRQLs for target metals *
Accuracy	Matrix Spike	Criteria listed in Table 28-4
Accuracy	Post Digestion Spike	Criteria listed in Table 28-4
Accuracy	Laboratory Control Sample	Criteria listed in Table 28-4
Accuracy	Preparation Blank	No analyte > CRQL
Precision	Interference Check Sample	< RL for RCRA metals

* See Table 15-2.

Matrix: Water

Analytical group or method: Semivolatile organics, SW-846 8270C

Concentration level: Low

Data Quality Indicator (DQI)	QC Sample or Measurement Performance Activity	Measurement Performance Criteria
Precision	Field Duplicates	≤30% RPD for analytes at least 5X reporting limit
Accuracy/Precision (laboratory)	Laboratory Control Sample and Laboratory Control Sample Duplicate	Criteria listed in Table 28-2
Sensitivity	Initial calibration and Form I for all environmental samples	Reporting limit 10 µg/L or better for most SVOCs
Accuracy	Internal Standards	Criteria listed in Table 28-2
Accuracy/Precision	Matrix Spike and Matrix Spike Duplicate	Criteria listed in Table 28-2
Accuracy	Surrogate Compounds	Criteria listed in Table 28-2
Accuracy	Lab Method Blank, Field (rinsate) Blank	< RL

QAPP Worksheet #13: Secondary Data Criteria and Limitations

Secondary data refer to historical data previously collected for the sites. The source(s) of the data, date of collection, planned uses, and limitations of the secondary data for each site are summarized in the following table.

Data Type	Source	Data Uses Relative to Current Project	Factors Affecting the Reliability of Data and Limitations on Data Use
GW, SW, SS, SB, Sediment, NAPL	Various, historical	Historical data to be used as needed based on limitations	The data is treated as screening-level qualitative measurements since full analytical QC data was not received with the data nor was there conclusive indication that full review was conducted.
Soil, GW,	CH2M HILL, OU1 RI	To help identify potential source areas and to help plan sampling locations	No limitation
Soil, GW, SW, Air, NAPL	CH2M HILL, OU1 SI	To help identify potential source areas and to help plan sampling locations	No limitation
Soil, GW, SW, PW	CH2M HILL, 2008–2009 SRI	To help identify potential source areas and to help plan sampling locations	No limitation
Soil	CH2M HILL, 2008–2009 soil sampling	To help identify potential source areas and to help plan sampling locations	No limitation
Soil, NAPL	CH2M HILL, 2010 soil sampling	To help identify potential source areas and to help plan sampling locations	No limitation
Soil, NAPL	CH2M HILL, 2011 soil sampling	To help identify potential source areas and to help plan sampling locations	No limitation
GW, Soil, Air	CH2M HILL, 2012 PDI	To help identify potential source areas and to help plan sampling locations	No limitation

Notes:
BERA— baseline ecological risk assessments
GW—groundwater
PCB—polychlorinated biphenyls
PDI—Pre-Design Investigation
RI— Remediation Investigation
SI—Supplemental Investigation
SRI—Supplemental Remediation Investigation
SVOC—semi-volatile organic compounds
TPH—total petroleum hydrocarbons
VOC—volatile organic compounds

QAPP Worksheets #14 and #16: Project Tasks and Schedule

The work scope involves the following tasks:

Activity	Responsible Party	Planned Start Date	Planned Completion Date	Deliverables	Deliverable Due Date
Work Plan Submittal	CH2M HILL	April 1, 2014	May 9, 2014	Cover Letter and UFP-QAPP, Baseline Groundwater Sampling	May 1, 2014
Procurement of Laboratory	Honeywell/CH2M HILL	May 9, 2014	May 18, 2014	Not Applicable	Not Applicable
Mobilization for sampling	CH2M HILL	June 1, 2014	June 1, 2014	Field notes	June 2, 2014
Sampling Event	CH2M HILL	June 1, 2014	June 6, 2014	Field notes	June 2, 2014
Laboratory Results Obtained	Accutest	June 27, 2014	June 27, 2014	Report of Analyses/Data package	End of June
Submit Report to USEPA	Honeywell/CH2M HILL	Fall 2014	End of 2014	Remedial Action Work Plan	Winter 2014

QAPP Worksheet #15: Project Action Limits and Laboratory-Specific Detection/Quantitation Limits

The following tables contain the list of target compounds or contaminants of concern that will be evaluated for this project. Due to the nature of the project, no project action limits have been specified or are required.

Matrix: Groundwater

Analytical method: Dissolved TAL Metals, Total VOCs, and Total SVOCs,

Concentration level (if applicable): Low

TABLE 15-1

Analyte	Project Action Limit	Laboratory Method Detection Limit (µg/L)	Laboratory Limit of Detection (µg/L)	Laboratory Limit of Quantitation (µg/L)
Aluminum (SW6010C)	NA	10.92	100	200
Antimony (SW6010C)	NA	1.84	5	6
Arsenic (SW6010C)	NA	1.48	3	5
Barium (SW6010C)	NA	0.36	10	200
Beryllium (SW6010C)	NA	0.17	1	2
Cadmium (SW6010C)	NA	0.24	2	3
Calcium (SW6010C)	NA	55.21	200	5000
Chromium (SW6010C)	NA	0.92	5	10
Cobalt (SW6010C)	NA	0.54	2	50
Copper (SW6010C)	NA	1.02	5	10
Iron (SW6010C)	NA	13.32	50	100
Lead (SW6010C)	NA	2.42	3	5
Magnesium (SW6010C)	NA	22.82	100	5000
Manganese (SW6010C)	NA	0.15	2	15
Nickel (SW6010C)	NA	1.55	4	10
Potassium (SW6010C)	NA	41.11	500	10000

TABLE 15-1

Analyte	Project Action Limit	Laboratory Method Detection Limit (µg/L)	Laboratory Limit of Detection (µg/L)	Laboratory Limit of Quantitation (µg/L)
Selenium (SW6010C)	NA	2.43	5	10
Silver (SW6010C)	NA	1.45	4	10
Sodium (SW6010C)	NA	57.88	100	10000
Thallium (SW6010C)	NA	1.32	2	5.0
Vanadium (SW6010C)	NA	0.72	4	50
Zinc (SW6010C)	NA	4.36	5	20
Aluminum (SW6020A)	NA	2.295	40	50
Antimony (SW6020A)	NA	0.291	2	4
Arsenic (SW6020A)	NA	0.083	2	4
Barium (SW6020A)	NA	0.149	1	2
Beryllium (SW6020A)	NA	0.059	1	2
Cadmium (SW6020A)	NA	0.106	4	6
Calcium (SW6020A)	NA	3.470	100	500
Chromium (SW6020A)	NA	0.060	6	8
Cobalt (SW6020A)	NA	0.066	0.5	1
Copper (SW6020A)	NA	0.334	4	8
Iron (SW6020A)	NA	2.363	25	50
Lead (SW6020A)	NA	0.033	2	3
Magnesium (SW6020A)	NA	3.603	250	500
Manganese (SW6020A)	NA	0.187	2	4
Nickel (SW6020A)	NA	0.197	6	8
Potassium (SW6020A)	NA	5.271	100	500
Selenium (SW6020A)	NA	0.346	1	2

TABLE 15-1

Analyte	Project Action Limit	Laboratory Method Detection Limit (µg/L)	Laboratory Limit of Detection (µg/L)	Laboratory Limit of Quantitation (µg/L)
Silver (SW6020A)	NA	0.057	1	2
Sodium (SW6020A)	NA	35.634	100	500
Thallium (SW6020A)	NA	0.112	1	2
Vanadium (SW6020A)	NA	0.126	2	3
Zinc (SW6020A)	NA	0.800	6	8
Mercury	NA	0.089	0.15	0.2
Acetone	NA	3.3	5	10
Benzene	NA	0.28	0.35	0.5
Bromobenzene	NA	0.25	0.5	5
Bromochloromethane	NA	0.42	1	5
Bromodichloromethane	NA	0.21	0.5	1
Bromoform	NA	0.3	0.5	2
Bromomethane	NA	0.56	1	2
2-Butanone (MEK)	NA	3.2	5	10
n-Butylbenzene	NA	0.39	1	2
sec-Butylbenzene	NA	0.48	0.5	2
tert-Butylbenzene	NA	0.25	0.5	2
Carbon tetrachloride	NA	0.23	1	1
Chlorobenzene	NA	0.35	0.5	1
Chloroethane	NA	0.39	1	1
Chloroform	NA	0.25	0.5	1
Chloromethane	NA	0.36	1	1
2-Chlorotoluene	NA	0.17	0.5	5

TABLE 15-1

Analyte	Project Action Limit	Laboratory Method Detection Limit (µg/L)	Laboratory Limit of Detection (µg/L)	Laboratory Limit of Quantitation (µg/L)
4-Chlorotoluene	NA	0.28	0.5	5
1,2-Dibromo-3-chloropropane	NA	1.3	2	5
Dibromochloromethane	NA	0.19	0.5	1
1,2-Dibromoethane	NA	0.16	0.5	1
1,2-Dichlorobenzene	NA	0.2	0.5	1
1,3-Dichlorobenzene	NA	0.31	0.5	1
1,4-Dichlorobenzene	NA	0.3	0.5	1
Dichlorodifluoromethane	NA	0.63	1	5
1,1-Dichloroethane	NA	0.26	0.5	1
1,2-Dichloroethane	NA	0.22	1	1
1,1-Dichloroethene	NA	0.34	0.5	1
cis-1,2-Dichloroethene	NA	0.24	0.5	1
trans-1,2-Dichloroethene	NA	0.38	0.5	1
1,2-Dichloropropane	NA	0.28	0.5	1
1,3-Dichloropropane	NA	0.23	0.5	2
2,2-Dichloropropane	NA	0.21	0.5	2
1,1-Dichloropropene	NA	0.17	0.5	2
cis-1,3-Dichloropropene	NA	0.15	0.5	1
trans-1,3-Dichloropropene	NA	0.21	0.5	1
Ethylbenzene	NA	0.21	0.25	0.5
Hexachlorobutadiene	NA	0.42	0.5	2
Isopropylbenzene	NA	0.22	0.5	1
p-Isopropyltoluene	NA	0.42	0.5	5

TABLE 15-1

Analyte	Project Action Limit	Laboratory Method Detection Limit (µg/L)	Laboratory Limit of Detection (µg/L)	Laboratory Limit of Quantitation (µg/L)
Methyl Tert Butyl Ether	NA	0.29	0.5	1
4-Methyl-2-pentanone (MIBK)	NA	1.5	5	5
Methylene bromide	NA	0.33	1	2
Methylene chloride	NA	0.86	1	2
Naphthalene	NA	0.25	2	5
n-Propylbenzene	NA	0.32	0.5	2
Styrene	NA	0.3	0.5	2
1,1,1,2-Tetrachloroethane	NA	0.21	0.5	5
1,1,2,2-Tetrachloroethane	NA	0.2	0.5	1
Tetrachloroethene	NA	0.25	0.5	1
Toluene	NA	0.44	0.5	1
1,2,3-Trichlorobenzene	NA	0.24	1	5
1,2,4-Trichlorobenzene	NA	0.22	0.5	5
1,1,1-Trichloroethane	NA	0.25	0.5	1
1,1,2-Trichloroethane	NA	0.21	0.5	1
Trichloroethene	NA	0.5	0.5	1
Trichlorofluoromethane	NA	0.33	1	5
1,2,3-Trichloropropane	NA	0.67	2	5
1,2,4-Trimethylbenzene	NA	0.23	1	2
1,3,5-Trimethylbenzene	NA	0.43	0.5	2
Vinyl chloride	NA	0.41	0.5	1
m,p-Xylene	NA	0.4	0.5	1
o-Xylene	NA	0.19	0.5	1

TABLE 15-1

Analyte	Project Action Limit	Laboratory Method Detection Limit (µg/L)	Laboratory Limit of Detection (µg/L)	Laboratory Limit of Quantitation (µg/L)
Xylene (total)	NA	0.19	0.5	1
2-Chlorophenol	NA	0.97	2.5	5
4-Chloro-3-methyl phenol	NA	1.8	2.5	5
2,4-Dichlorophenol	NA	1.2	2	2
2,4-Dimethylphenol	NA	1.5	2.5	5
2,4-Dinitrophenol	NA	17	20	20
4,6-Dinitro-o-cresol	NA	0.99	2.5	20
2-Methylphenol	NA	1	2	2
3&4-Methylphenol	NA	0.93	2	2
2-Nitrophenol	NA	1.5	2.5	5
4-Nitrophenol	NA	5.2	10	10
Pentachlorophenol	NA	1.4	2.5	10
Phenol	NA	1.3	2	2
2,3,4,6-Tetrachlorophenol	NA	0.94	2.5	5
2,4,5-Trichlorophenol	NA	1.6	2.5	5
2,4,6-Trichlorophenol	NA	1.3	2.5	5
Acenaphthene	NA	0.26	0.5	1
Acenaphthylene	NA	0.23	0.5	1
Acetophenone	NA	0.29	0.5	2
Anthracene	NA	0.29	0.5	1
Atrazine	NA	0.49	0.5	2
Benzaldehyde	NA	3.3	5	5
Benzo(a)anthracene	NA	0.23	0.5	1

TABLE 15-1

Analyte	Project Action Limit	Laboratory Method Detection Limit (µg/L)	Laboratory Limit of Detection (µg/L)	Laboratory Limit of Quantitation (µg/L)
Benzo(a)pyrene	NA	0.23	0.5	1
Benzo(b)fluoranthene	NA	0.46	0.5	1
Benzo(g,h,i)perylene	NA	0.32	0.5	1
Benzo(k)fluoranthene	NA	0.51	1	1
4-Bromophenyl phenyl ether	NA	0.36	0.5	2
Butyl benzyl phthalate	NA	0.29	0.5	2
1,1'-Biphenyl	NA	0.3	0.5	1
2-Chloronaphthalene	NA	0.3	0.5	2
4-Chloroaniline	NA	0.53	2	5
Carbazole	NA	0.36	0.5	1
Caprolactam	NA	0.69	2	2
Chrysene	NA	0.29	0.5	1
bis(2-Chloroethoxy)methane	NA	0.31	0.5	2
bis(2-Chloroethyl)ether	NA	0.31	0.5	2
bis(2-Chloroisopropyl)ether	NA	0.45	0.5	2
4-Chlorophenyl phenyl ether	NA	0.31	0.5	2
2,4-Dinitrotoluene	NA	0.43	0.5	1
2,6-Dinitrotoluene	NA	0.46	0.5	1
3,3'-Dichlorobenzidine	NA	0.36	0.5	2
1,4-Dioxane	NA	0.27	0.5	1
Dibenzo(a,h)anthracene	NA	0.38	0.5	1
Dibenzofuran	NA	0.27	0.5	5
Di-n-butyl phthalate	NA	0.56	1	2

TABLE 15-1

Analyte	Project Action Limit	Laboratory Method Detection Limit (µg/L)	Laboratory Limit of Detection (µg/L)	Laboratory Limit of Quantitation (µg/L)
Di-n-octyl phthalate	NA	0.31	0.5	2
Diethyl phthalate	NA	0.33	0.5	2
Dimethyl phthalate	NA	0.28	0.5	2
bis(2-Ethylhexyl)phthalate	NA	0.59	1	2
Fluoranthene	NA	0.32	0.5	1
Fluorene	NA	0.28	0.5	1
Hexachlorobenzene	NA	0.34	0.5	1
Hexachlorobutadiene	NA	0.51	1	1
Hexachlorocyclopentadiene	NA	7.1	10	10
Hexachloroethane	NA	0.55	1	2
Indeno(1,2,3-cd)pyrene	NA	0.37	0.5	1
Isophorone	NA	0.27	0.5	2
2-Methylnaphthalene	NA	0.38	1	1
2-Nitroaniline	NA	1.1	5	5
3-Nitroaniline	NA	1.3	5	5
4-Nitroaniline	NA	1.7	5	5
Naphthalene	NA	0.26	0.5	1
Nitrobenzene	NA	0.42	0.5	2
N-Nitroso-di-n-propylamine	NA	0.3	0.5	2
N-Nitrosodiphenylamine	NA	0.31	0.5	5
Phenanthrene	NA	0.29	0.5	1
Pyrene	NA	0.27	0.5	1
1,2,4,5-Tetrachlorobenzene	NA	0.31	0.5	2

QAPP Worksheet #17: Sampling Design and Rationale

Sampling design and rationale were developed to evaluate baseline groundwater conditions across the site in various strata. The wells were picked to encompass all subsurface units and at various locations throughout OU1. Sample locations, purpose, and methods are specified in Table 17-1 and shown in Figure 1.

Baseline and long-term monitoring associated with the HCAA remedy will be conducted as part of a separate scope. Installation of new monitoring wells for sampling and monitoring of near-shore conditions to support SRB design following ISS at NZ-2 will be part of the OU1 remedial design.

Sampling

Groundwater samples for analytical testing will be collected using low-flow sampling methods in accordance the original field sampling plan (Parsons, 2005a) and as described in the 1998 “USEPA Region II Groundwater Sampling Procedure Low Stress (Low Flow) Purging and Sampling”. Groundwater samples will be collected from the eleven monitoring wells and samples will be analyze for the selection of the following as per Table 17-1:

- Dissolved TAL metals using laboratory EPA Method 6010B/7470B
- Volatile Organic Compounds using laboratory EPA Method 8260B
- Semi-volatile organic compounds using laboratory EPA Method 8270C

TABLE 17-1
Groundwater Monitoring Wells for Sitewide Preremedy Sampling

Location ID	Screened Depth (ft bgs)	Stratigraphy	Purpose/Type	Parameters		
				Dissolved TAL Metals, Method 6010B/7470B	VOCs, Method 8260B	SVOCs, Method 8270C
Upgradient/Cross Gradient						
MW-125	5–15	Shallow Unconfined	Upgradient—All Constituents	X	X	X
ACMW-3	1.75–21.75	Shallow Unconfined	Cross-gradient of HCAA. Confirms northern CEA boundary.	X		
MW-101DS	38–48	Deep Sand	Upgradient Deep Sand (below vertical extent of OU1). Comparison point for MW-107DS.	X	X	X
Within OU1						
MW-114A	3–13	Shallow Unconfined	Near ISS areas, within OU1. Monitor for potential change due to ISS.	X	X	X
MW-114B	15–25	Shallow Unconfined	Near ISS areas, within OU1. Monitor for potential change due to ISS.	X	X	X
MW-F	7–17	Shallow Unconfined	Near CEA boundary to the north along the shoreline.	X	X	X
TW-06	17–27	Shallow Unconfined	Monitor for potential effects in deep groundwater concentrations due to stacked area ISS.	X	X	X
MW-106A	3–13	Shallow Unconfined	Establish baseline conditions adjacent to NZ-2 ISS on the south side, nearshore.	X	X	X
Downgradient/Outside OU1						
MW-107DS	52–62	Deep Sand	Downgradient Deep Sand (below vertical extent of OU1). Sentry for underlying stratigraphy within lateral extent of CEA/OU1.	X	X	X
MW-124	6–16	Shallow Unconfined	Monitor west boundary of CEA	X	X	X
MW-132	4–14	Shallow Unconfined	Laterally Downgradient monitoring—organics. Confirms southern CEA boundary.	X	X	X

QAPP Worksheet #18: Sampling Locations and Methods

Sampling locations and methods are outlined in the following subsections.

Sample ID	Matrix	Depth (ft bgs)	Type	Analyte/Analytical Group	Sampling SOP	Comments
MW-125-MMYY	Groundwater	Not Applicable	Upgradient/Cross Gradient	As per Worksheet #17	GW Sampling SOP	Decon sampling equipment as per SOP #002
ACMW-3-MMYY	Groundwater	Not Applicable	Upgradient/Cross Gradient	As per Worksheet #17	GW Sampling SOP	Decon sampling equipment as per SOP #002
MW-101DS-MMYY	Groundwater	Not Applicable	Upgradient/Cross Gradient	As per Worksheet #17	GW Sampling SOP	Decon sampling equipment as per SOP #002
MW-114A-MMYY	Groundwater	Not Applicable	Within OU1	As per Worksheet #17	GW Sampling SOP	Decon sampling equipment as per SOP #002
MW-114B-MMYY	Groundwater	Not Applicable	Within OU1	As per Worksheet #17	GW Sampling SOP	Decon sampling equipment as per SOP #002
MW-F-MMYY	Groundwater	Not Applicable	Within OU1	As per Worksheet #17	GW Sampling SOP	Decon sampling equipment as per SOP #002
TW-06-MMYY	Groundwater	Not Applicable	Within OU1	As per Worksheet #17	GW Sampling SOP	Decon sampling equipment as per SOP #002
MW-106A-MMYY	Groundwater	Not Applicable	Within OU1	As per Worksheet #17	GW Sampling SOP	Decon sampling equipment as per SOP #002
MW-107DS-MMYY	Groundwater	Not Applicable	Downgradient/ Outside OU1	As per Worksheet #17	GW Sampling SOP	Decon sampling equipment as per SOP #002
MW-124-MMYY	Groundwater	Not Applicable	Downgradient/ Outside OU1	As per Worksheet #17	GW Sampling SOP	Decon sampling equipment as per SOP #002
MW-132-MMYY	Groundwater	Not Applicable	Downgradient/ Outside OU1	As per Worksheet #17	GW Sampling SOP	Decon sampling equipment as per SOP #002
MW-124-Dup-MMYY	Groundwater	Not Applicable	Quality Control/ Duplicate	As per Worksheet #17	GW Sampling SOP	Decon sampling equipment as per SOP #002
MW-107DS-Dup-MMYY	Groundwater	Not Applicable	Quality Control/ Duplicate	As per Worksheet #17	GW Sampling SOP	Decon sampling equipment as per SOP #002
MW-101DS -MS	Groundwater	Not Applicable	Quality Control	As per Worksheet #17	GW Sampling SOP	Decon sampling equipment as per SOP #002
MW-101DS -MSD	Groundwater	Not Applicable	Quality Control	As per Worksheet #17	GW Sampling SOP	Decon sampling equipment as per SOP #002

Sample ID	Matrix	Depth (ft bgs)	Type	Analyte/Analytical Group	Sampling SOP	Comments
FB-MMYY	Blank	Not Applicable	Field Blank	As per Worksheet #17	GW Sampling SOP	Decon sampling equipment as per SOP #002
EB-MMYY	Blank	Not Applicable	Equipment Blank	As per Worksheet #17	GW Sampling SOP	Decon sampling equipment as per SOP #002

The "MMYY" listed in the Sample IDs will be replaced with the appropriate month and year nomenclature based on the sampling date. Actual amount of QC samples (Equipment Blank, Duplicates, and MS/MSD) will be based on total amount of samples collected in accordance with Worksheet #20

QAPP Worksheets #19 and #30: Sample Containers, Preservation, and Hold Times

The sampling objectives for analysis by an offsite laboratory are described below. The project specific target analytes and required methods are defined in the below table along with the appropriate bottleware to be used for each analysis.

Laboratory (name, sample receipt address, POC, e-mail, and phone numbers): Accutest Laboratories New Jersey, Inc., 2235 US Highway 130, Dayton, NJ 08810, POC: Kristin Beebe, 732-329-0200, Kristinb@accutest.com

List any required accreditations/certifications: Laboratory has current NELAC and/or New Jersey certification.

Back-up Laboratory: None

Sample delivery method: Courier pickup

Analytical Group	Matrix	Method/SOP	Containers (Number, Size, and Type per Sample)	Preservation Requirements	Preparation Holding Time	Analytical Holding Time	Data Package Turnaround
Dissolved Metals	Water	SW6010C/ SOP EMA227-08 SW6020A/ SOP EMA226-07 SW7470A/ SOP EMA215-15	500 ml Polyethylene	HNO_3, pH<2, 4°C after field filtration	NA	180 days (28 days for mercury)	21-day
VOCs	Water	SW5030B/8260B/ SOP EMS8260B-24	Three 40 mL glass vial	HCl, pH<2, 4°C	NA	14 days	21-day
SVOCs	Water	SW3550B/8270D/ SOP EMS8270D-06	Two 1-L amber glass	4°C	7 days	40 days	21-day

QAPP Worksheet #20: Field QC Summary

Quality control samples will be collected to monitor accuracy, precision, and the presence of field contamination for analytical methods to be performed in the offsite laboratory. The frequency of collection of the quality control samples is outlined below.

Matrix	Analytical Group[1]	Analysis	Field Samples	Field Duplicates	Matrix Spikes	Matrix Spike Duplicates	Field Blanks	Equipment Blanks	Trip Blanks	Total No. of Samples Analyzed
Liquid	Groundwater	As per Worksheet #18	11	2	1	1	3	3	3	13

[1] The sediment and groundwater field and specialty analyses data will not be validated; information for these methods is not included Worksheets 12, 19/30, 23–25, 28, 34–37.

- **Trip Blanks**—A trip blank will be prepared before the laboratory sends the sample containers. The trip blank will consist of a 40-ml volatile organic analytic vial containing distilled, deionized water, which accompanies the other aqueous sample bottles into the field and back to the laboratory. A trip blank will be included with each shipment of water samples for volatiles analysis. The trip blank will be analyzed for the same volatile organic compounds as the samples to detect any contamination from sampling and transport, and internal laboratory procedures.
- **Equipment Blanks**—Equipment blanks will be taken at a frequency of one per decontamination event, maximum of one per day sampling equipment type, minimum of one per week. An equipment blank is used to assess the effectiveness of the decontamination procedures for sampling equipment. It is a sample of deionized, distilled water provided by the laboratory, which has passed through a decontaminated bailer or other sampling apparatus. It is usually collected as a last step in the decontamination procedure, before taking an aqueous sample. The equipment blank may be analyzed for all of the parameters of interest. An equipment blank is not needed if clean disposable sampling equipment is utilized.
- **Field Blank**—A blank used to provide information about contaminants that may be introduced during sample collection, storage, and transport; also a clean sample exposed to sampling conditions, transported to the laboratory, and treated as an environmental sample..
- **Duplicates** will consist of:
  - Field Duplicate—To assess the representativeness of the sampling methods, field duplicates will be collected at a minimum frequency of one per 10 environmental samples per matrix.
  - Matrix Spike/Matrix Spike Duplicate—MS/MSD samples will be taken at a frequency of one pair per 20 field samples. These samples are used to assess the effect of the sample matrix on the recovery of target analytes.

QAPP Worksheet #21: Field SOPs

The following Field SOPs will be used for the tests conducted above. Actual SOPs are included as Attachment 1 of this UFP-QAPP.

SOP#	Title, Revision, Date, and URL (if Available)	Originating Organization	SOP Option or Equipment Type (if SOP Provides Different Options)	Modified for Project? Y/N	Comments
GW Sampling SOP	Groundwater Sampling Procedure—Low Stress (Low Flow) Purging and Sampling	U.S. Environmental Protection Agency—Region 2	Applies to all low-flow sampling procedures	No	
002	Equipment Decontamination, 7/16/2012	CH2M HILL	Applies to all non-disposable equipment used for sampling	No	

QAPP Worksheet #22: Field Equipment Calibration, Maintenance, Testing, and Inspection

Field Equipment	Activity	SOP Reference	Title or Position of Responsible Person	Frequency	Acceptance Criteria	Corrective Action
PID	Per Manual	Per Manual	Field Team Lead	Per Manual	Per Manual	Per Manual
LaMotte Turbidometer 2020	Per Manual	Per Manual	Field Team Lead	Per Manual	Per Manual	Per Manual
pH Monitor (included with YSI)	Per Manual	Per Manual	Field Team Lead	Per Manual	Per Manual	Per Manual
YSI 600	Per Manual	Per Manual	Field Team Lead	Per Manual	Per Manual	Per Manual

The above manuals are kept within the project files and can be found at the below links:

- PID—http://www.raesystems.com/sites/default/files/downloads/FeedsEnclosure-MiniRAE3000_Pocket_Reference_0.pdf
- LaMotte Turbidometer 2020—http://www.lamotte.com/images/pdf/instructions/1970-MN.pdf
- YSI 600—https://www.ysi.com/media/pdfs/069300-YSI-6-Series-Manual-RevH.pdf

The manuals listed above are included as attachments to this UFP-QAPP.

QAPP Worksheet #23: Analytical SOPs

Laboratory must have current NELAC and/or New Jersey certification. The following Analytical SOPs are included as Attachment 2 of this UFP-QAPP.

SOP#	Title, Revision Date, and/or Number	Definitive or Screening Data	Analytical Group	Instrument	Organization Performing Analysis	Modified for Project Work? (Y/N)
EMS8270D-06	Method SW8270D, Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry, Rev 6 6/11/2013	Definitive	Semivolatiles	GC/MS	Accutest Laboratories New Jersey, Inc., Dayton, NJ	No
EMS8260B-24	Method SW8260B, Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry, Rev 24 1/29/2014	Definitive	Volatiles	GC/MS	Accutest Laboratories New Jersey, Inc., Dayton, NJ	No
EMA227-08	Metals by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP) Using Solid State ICP, Rev 8 8/27/2013	Definitive	Metals	ICP	Accutest Laboratories New Jersey, Inc., Dayton, NJ	No
EMA226-07	Metals by Inductively Coupled Plasma—Mass Spectrometry (ICP-MS), Rev 7 4/12/13	Definitive	Metals	ICP-MS	Accutest Laboratories New Jersey, Inc. Dayton, NJ	No
EMP070-15	Digestion of Non-Potable Waters for ICP or ICP-MS Analysis, Rev 15 8/8/13	Definitive	Metals	Digestion Block	Accutest Laboratories New Jersey, Inc. Dayton, NJ	No
EMA215-15	Cold Vapor Analysis of Mercury for Water Samples, Rev 15 9/25/2013	Definitive	Mercury	Cold Vapor AA	Accutest Laboratories New Jersey, Inc. Dayton, NJ	No

QAPP Worksheet #24: Analytical Instrument Calibration

Identify all analytical instrumentation that requires calibration and provide the SOP reference number for each. In addition, document the frequency, acceptance criteria, and corrective action requirements on the worksheet.

Instrument	Calibration Procedure	Frequency of Quality Control	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference
Thermo 6500 ICP	Initial Blank + 3 non zero std's	Daily	Correlation Coefficient R ≥ 0.995	Instrument maintenance, standard, inspection, recalibration	Laboratory Analyst	EMA227-08
	ICV	Beginning of run	≤ 10% Diff			
	CCV	Beginning of run, every 10 samples and end of run	≤ 10% Diff			
Agilent 7700 ICPMS	Tune	Every 1-2 days	RSD of min 4 replicates < 5% for all elements in tune solution Resolution < 0.9 amu full width at 10% peak height Mass Calibration < 0.1 amu	Retune Instrument	Laboratory Analyst	EMA226-07
	Initial cal, blank + 3 non zero standards	Daily	R > 0.995	Perform Instrument Maintenance, Check or reprep Standards, Recalibrate instrument		
	Initial Calibration Verification (Second Source Standard)	After ICAL	+ 10% of true value	Reanalyze ICV, Recalibrate instrument		
	Continuing Calibration Verification	After ICV, every 10 samples and end of run	+ 10% of true value	Reanalyze CCV, Recalibrate & Reanalyze affected samples		

Instrument	Calibration Procedure	Frequency of Quality Control	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference
	Low Level Calibration Check	After ICV and end of run	+ 20% of true value	Reanalyze LLCC , Perform Instrument Maintenance, Check or reprep Standards, Recalibrate instrument		
	Interference Check Standard (ICSA/ICASB)	After CCV, and every 12 hours	ICSA < LOD ICSAB +/- 20% of true value	Rerun ICSA/ICSAB, and all affected samples		
GC/MS HP5890/5970, HP6890/5973, Agilent 6890/5973	Initial calibration	Daily	Initial ≤ 15% RSD	Perform Maintenance, Check Standards, Recalibrate, Reanalyze	Assigned Lab personnel	EMS8260B-24
	Initial Calibration Verification	After ICAL	ICV ≤ 20% Diff			
	Continuing Calibration Verification	After ICV, every 10 samples and end of run	CCV ≤ 20% Diff			
GC/MS HP5890/5972 HP6890/5973 Agilent 6890/5975	Initial calibration	Daily	Initial < 20% RSD; Minimum RF's	Perform Maintenance, Check Standards, Recalibrate, Reanalyze	Assigned Lab personnel	EMS8270D-06
	Initial Calibration Verification	After ICAL	ICV < 30% Diff			
	Continuing Calibration Verification	After ICV, every 10 samples and end of run	CCV < 20% Diff			
Leeman Hydra II AA	Initial Blank + 5 non zero std's	Daily	Correlation Coefficient R ≥ 0.995	Instrument maintenance, standard, inspection, recalibration	Assigned Lab personnel	EMA215-15
	Initial Calibration Verification	After ICAL	≤ 10% Diff			
	Continuing Calibration Verification	After ICV, every 10 samples and end of run	≤ 20% Diff			

* Data for these specialty analyses will not be validated.

QAPP Worksheet #25: Analytical Instrument and Equipment Maintenance, Testing, and Inspection

Instrument/ Equipment	Maintenance Activity	Testing Activity	Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	Responsible Person	SOP Reference[1]
Thermo 6500 ICP	Torch, nebulizer, spray chamber, autosampler, pump tubing maintenance	SW-846 6010C	Check connections, flush lines, clean nebulizer	Daily or as needed	Passing calibration	Perform maintenance, check standards, recalibrate	Laboratory Analyst	EMA227-08
Agilent 7700X	Clean/replace torch, clean cone Clean/replace nebulizer, change pump tubing	SW846 6020A	Rf Generator power, nebulizer pressure, turbopump speed	Daily as needed	Passing tune, ICV and CCV	Perform Maintenance, Check Standards, Recalibrate, Reanalyze	Laboratory Analyst	EMA226-07
Leeman Hydra II AA	Pump tubing, absorption cell and lens cleaning	SW-846 7470A/7471A	Check connections, flush sample lines	Daily or as needed	Passing calibration	Perform maintenance, check standards, recalibrate	Laboratory Analyst	EMA215-15
GC/MS HP5890/5970 HP6890/5973 Agilent 6890/5973	Clean/bake sample lines and trap, clip/replace column, clean source	SW846 8260B	Pass BFB tune, Continuing Calibration	Daily or as needed	BFB Criteria CCV < 20% Diff	Perform Maintenance, Check Standards, Recalibrate, Reanalyze	Assigned lab personnel	EMS8260B-24
GC/MS HP5890/5972 HP6890/5973 Agilent 6890/5975	Clean/bake sample lines and trap, clip/replace column, clean source	SW846 8270D	Pass DFTPP tune, Continuing Calibration	Daily or as needed	DFTPP Criteria CCV < 20% Diff	Perform Maintenance, Check Standards, Recalibrate, Reanalyze	Assigned lab personnel	EMS8270D-06

QAPP Worksheet #26 and #27: Sample Handling, Custody, and Disposal

Sampling organization: Various

Laboratory: Accutest

Method of sample delivery (shipper/carrier): Federal Express—Priority Overnight

Number of days from reporting until sample disposal: Minimum 30 days after final report sent to the client

Activity	Organization and Title or Position of Person Responsible for the Activity	SOP Reference
Sample labeling	Field Team Lead, CH2M HILL	As Per COC SOP (attached)
Chain-of-custody form completion	Field Team Lead, CH2M HILL	As Per COC SOP (attached)
Packaging	Field Team Lead, CH2M HILL	As Per Packaging and Shipping Procedures SOP (attached)
Shipping coordination	Field Team Lead, CH2M HILL	As Per Packaging and Shipping Procedures SOP (attached)
Sample receipt, inspection, and log-in	Nick Popow, Supervisor, Receiving/Accutest	Accutest SOP# EPM004-04
Sample custody and storage	Dave Hukele, Sample Custodian/Accutest	Accutest SOP# ESM001-09
Sample disposal	Robert MacLean, Accutest	Accutest SOP# EHS004-04

Collecting data of known quality begins at the point of sample collection. Legally defensible data are generated by adhering to proven evidentiary procedures. These procedures are outlined in the following sections and must be followed to preserve and ensure the integrity of all samples from the time of collection through analysis. Sample custody records must be maintained both in the field and in the subcontractor laboratory. A sample is considered to be in someone's custody if it is either in his or her physical possession or view, locked up, or kept in a secured and restricted area. Until shipment, sample custody will be the responsibility of the sampling team leader.

Chain-of-custody records document sample collection and shipment to the laboratory. A chain-of-custody form will be completed for each sampling event. The original copy will be provided to the laboratory with the sample shipping cooler, and a copy will be retained in the field documentation files. The chain-of-custody form will identify the contents of each shipment and maintain the custodial integrity of the samples. All chain-of-custody forms will be signed and dated by the responsible sampling team personnel. The "relinquished by" box will be signed by the responsible sampling team personnel, and the date, time, and air bill number will be noted on the chain-of-custody form. The laboratory will return the executed copy of the chain-of-custody with the hardcopy report.

The shipping coolers containing the samples will be sealed with a custody seal any time the coolers are not in an individual's possession or view before shipping. All custody seals will be signed and dated by the responsible sampling team personnel.

At a minimum, the chain-of-custody form must contain:

- Site name.
- Project Manager, Project Chemist, and Data Manager names, telephone numbers, and fax numbers.
- Unique sample identification.
- Date and time of sample collection.
- Source of sample (including name, location, sample type, and matrix).
- Number of containers.
- Designation of MS/MSD.
- Preservative used.
- Analyses required.
- Name of sampler.
- Custody transfer signatures and dates and times of sample transfer from the field to transporters and to the laboratories.
- Bill of lading or transporter tracking number (if applicable).
- Turnaround time.
- Lab name, address, and contact information.
- Any special instructions.

Erroneous entries on chain-of-custody records will be corrected by drawing a line through the error and entering the corrected information. The person performing the correction will date and initial each change made on the chain-of-custody form.

Laboratory Sample Custody Procedures (receipt of samples, archiving, disposal): A custodian at the laboratory will accept custody of the shipped samples, and check them for discrepancies, proper preservation, integrity, etc. If noted, issues will be forwarded to the laboratory project or laboratory manager for corrective action; Earth Tech will be notified and will be involved in decisions on corrective action. The sample custodian will relinquish custody to the appropriate department for analysis. A "Condition upon Receipt" or similar form will be completed by the laboratory and will be included in the analytical data package.

Disposal of the samples will occur only after analyses and QA/QC checks are completed, and 60 days after issuance of analytical report.

STANDARD OPERATING PROCEDURE

Chain-of-Custody

I Purpose

The purpose of this SOP is to provide information on chain-of-custody procedures to be used for project work.

II Scope

This procedure describes the steps necessary for transferring samples through the use of Chain-of-Custody Records. A Chain-of-Custody Record is required, without exception, for the tracking and recording of samples collected for on-site or off-site analysis (chemical or geotechnical) during program activities (except wellhead samples taken for measurement of field parameters). Use of the Chain-of-Custody Record Form creates an accurate written record that can be used to trace the possession and handling of the sample from the moment of its collection through analysis. This procedure identifies the necessary custody records and describes their completion. This procedure does not take precedence over region specific or site-specific requirements for chain-of-custody.

III Definitions

Chain-of-Custody Record Form - A Chain-of-Custody Record Form is a printed two-part form that accompanies a sample or group of samples as custody of the sample(s) is transferred from one custodian to another custodian. One copy of the form must be retained in the project file.

Custodian - The person responsible for the custody of samples at a particular time, until custody is transferred to another person (and so documented), who then becomes custodian. A sample is under one's custody if:

- It is in one's actual possession.
- It is in one's view, after being in one's physical possession.
- It was in one's physical possession and then he/she locked it up to prevent tampering.
- It is in a designated and identified secure area.

Sample - A sample is physical evidence collected from a facility or the environment, which is representative of conditions at the point and time that it was collected.

IV. Procedures

The term "chain-of-custody" refers to procedures which ensure that evidence presented in a court of law is valid. The chain-of-custody procedures track the evidence from the time and place it is first obtained to the courtroom, as well as providing security for the evidence as it is moved and/or passed from the custody of one individual to another.

Chain-of-custody procedures, recordkeeping, and documentation are an important part of the management control of samples. Regulatory agencies must be able to provide the chain-of-possession and custody of any samples that are offered for evidence, or that form the basis of analytical test results introduced as evidence. Written procedures must be available and followed whenever evidence samples are collected, transferred, stored, analyzed, or destroyed.

Sample Identification

The method of identification of a sample depends on the type of measurement or analysis performed. When *in situ* measurements are made, the data are recorded directly in bound logbooks or other field data records with identifying information.

Information which shall be recorded in the field logbook, when in-situ measurements or samples for laboratory analysis are collected, includes:

- Field Sampler(s),
- Contract Number,
- Project Sample Number,
- Sample location or sampling station number,
- Date and time of sample collection and/or measurement,
- Field observations,
- Equipment used to collect samples and measurements, and
- Calibration data for equipment used

Measurements and observations shall be recorded using waterproof ink.

Sample Label

Samples, other than for *in situ* measurements, are removed and transported from the sample location to a laboratory or other location for analysis. Before removal, however, a sample is often divided into portions, depending upon the analyses to be performed. Each portion is preserved in accordance with the Sampling and Analysis Plan. Each sample container is identified by a sample label (see Attachment A). Sample labels are provided, along with sample containers, by the analytical laboratory. The information recorded on the sample label includes:

- Project Number.
- Station Location - The unique sample number identifying this sample.
- Date - A six-digit number indicating the day, month, and year of sample collection (e.g., 08/21/12).

- Time - A four-digit number indicating the 24-hour time of collection (for example: 0954 is 9:54 a.m., and 1629 is 4:29 p.m.).
- Medium - Water, soil, sediment, sludge, waste, etc.
- Sample Type - Grab or composite.
- Preservation - Type and quantity of preservation added.
- Analysis - VOA, BNAs, PCBs, pesticides, metals, cyanide, other.
- Sampled By - Printed name of the sampler.
- Remarks - Any pertinent additional information.

Using only the work assignment number of the sample label maintains the anonymity of sites. This may be necessary, even to the extent of preventing the laboratory performing the analysis from knowing the identity of the site (e.g., if the laboratory is part of an organization that has performed previous work on the site). The field team should always follow the sample ID system prepared by the project EIS and reviewed by the Project Manager.

Chain-of-Custody Procedures

After collection, separation, identification, and preservation, the sample is maintained under chain-of-custody procedures until it is in the custody of the analytical laboratory and has been stored or disposed.

Field Custody Procedures

- Samples are collected as described in the site Sampling and Analysis Plan. Care must be taken to record precisely the sample location and to ensure that the sample number on the label matches the Chain-of-Custody Record exactly.

- A Chain-of-Custody Record will be prepared for each individual cooler shipped and will include ***only*** the samples contained within that particular cooler. The Chain-of-Custody Record for that cooler will then be sealed in a zip-log bag and placed in the cooler prior to sealing. This ensures that the laboratory properly attributes trip blanks with the correct cooler and allows for easier tracking should a cooler become lost during transit.

- The person undertaking the actual sampling in the field is responsible for the care and custody of the samples collected until they are properly transferred or dispatched.

- When photographs are taken of the sampling as part of the documentation procedure, the name of the photographer, date, time, site location, and site description are entered sequentially in the site logbook as photos are taken. Once downloaded to the server or developed, the electronic files or photographic prints shall be serially numbered, corresponding to the logbook descriptions; photographic prints will be stored in the project files. To identify sample

locations in photographs, an easily read sign with the appropriate sample location number should be included.

- Sample labels shall be completed for each sample, using waterproof ink unless prohibited by weather conditions (e.g., a logbook notation would explain that a pencil was used to fill out the sample label if the pen would not function in freezing weather.)

Transfer of Custody and Shipment

Samples are accompanied by a Chain-of-Custody Record Form. **A Chain-of-Custody Record Form must be completed for each cooler and should include only the samples contained within that cooler**. A Chain-of-Custody Record Form example is shown in Attachment B. When transferring the possession of samples, the individuals relinquishing and receiving will sign, date, and note the time on the Record. This Record documents sample custody transfer from the sampler, often through another person, to the analyst in the laboratory. The Chain-of-Custody Record is filled out as given below:

- Enter header information (project number, samplers, and project name).

- Enter sample specific information (sample number, media, sample analysis required and analytical method grab or composite, number and type of sample containers, and date/time sample was collected).

- Sign, date, and enter the time under "Relinquished by" entry.

- Have the person receiving the sample sign the "Received by" entry. If shipping samples by a common carrier, print the carrier to be used in this space (i.e., Federal Express).

- If a carrier is used, enter the airbill number under "Remarks," in the bottom right corner;

- Place the original (top, signed copy) of the Chain-of-Custody Record Form in a plastic zipper-type bag or other appropriate sample-shipping package. Retain the copy with field records.

- Sign and date the custody seal, a 1-inch by 3-inch white paper label with black lettering and an adhesive backing. Attachment C is an example of a custody seal. The custody seal is part of the chain-of-custody process and is used to prevent tampering with samples after they have been collected in the field. Custody seals shall be provided by the analytical laboratory.

- Place the seal across the shipping container opening (front and back) so that it would be broken if the container were to be opened.

- Complete other carrier-required shipping papers.

The custody record is completed using waterproof ink. Any corrections are made by drawing a line through and initialing and dating the change, then entering the correct information. Erasures are not permitted.

Common carriers will usually not accept responsibility for handling Chain-of-Custody Record Forms; this necessitates packing the record in the shipping container (enclosed with other documentation in a plastic zipper-type bag). As long as custody forms are sealed inside the shipping container and the custody seals are intact, commercial carriers are not required to sign the custody form.

The laboratory representative who accepts the incoming sample shipment signs and dates the Chain-of-Custody Record, completing the sample transfer process. It is then the laboratory's responsibility to maintain internal logbooks and custody records throughout sample preparation and analysis.

V Quality Assurance Records

Once samples have been packaged and shipped, the Chain-of-Custody copy and airbill receipt become part of the quality assurance record.

VI Attachments

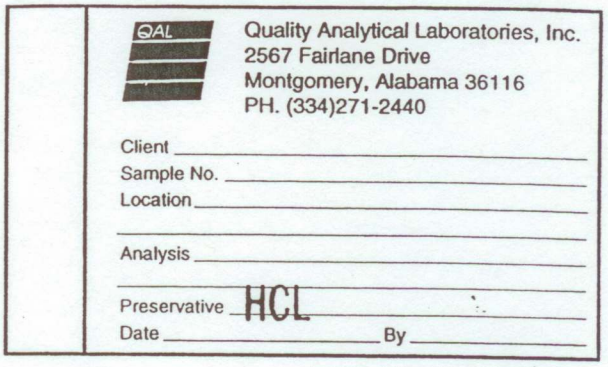
A. Sample Label
B. Chain of Custody Form
C. Custody Seal

VII References

USEPA. *User's Guide to the Contract Laboratory Program*. Office of Emergency and Remedial Response, Washington, D.C. (EPA/540/P-91/002), January 1991.

Attachment A

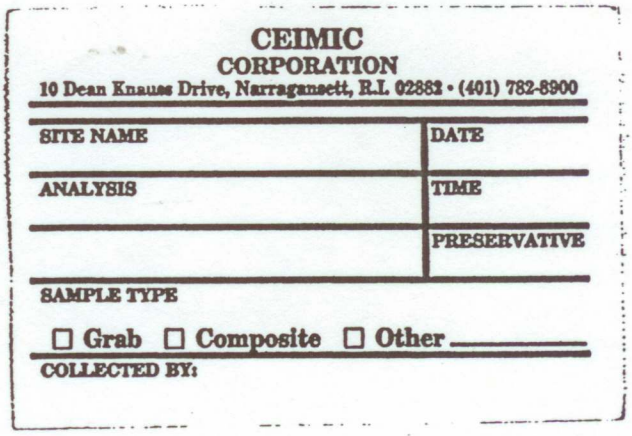
Example Sample Label



QAL

Quality Analytical Laboratories, Inc.
2567 Fairlane Drive
Montgomery, Alabama 36116
PH. (334)271-2440

Client _____
Sample No. _____
Location _____
_____
Analysis _____
_____
Preservative HCL
Date _____ By _____



CEIMIC
CORPORATION
10 Dean Knauss Drive, Narragansett, R.I. 02882 • (401) 782-8900

SITE NAME	DATE
ANALYSIS	TIME
	PRESERVATIVE

SAMPLE TYPE

☐ Grab ☐ Composite ☐ Other _____

COLLECTED BY:

Attachment B

Example Chain-of-Custody Record

CH2M HILL

APPLIED SCIENCES LABORATORY

CHAIN OF CUSTODY RECORD AND AGREEMENT TO PERFORM SERVICES

CH2M Hill Project # ☐☐☐☐☐☐☐☐.☐☐.☐☐

Purchase Order #

Project Name

Company Name CH2M HILL Office

Project Manager & Phone #
Mr. [ ]
Ms. [ ]
Dr. [ ]

Report Copy to:

Requested Completion Date:

Sampling Requirements: SDWA ☐ NPDES ☐ RCRA ☐ OTHER ____

Sample Disposal: Dispose ☐ Return ☐

Sampling Date	Sampling Time	Type COMP	Type GRAB	Matrix WATER	Matrix SOIL	Matrix AIR	CLIENT SAMPLE ID (9 CHARACTERS)	# OF CONTAINERS

LAB TEST CODES

ANALYSES REQUESTED

SHADED AREA– FOR LAB USE ONLY

Lab 1 #

Lab 2 #

Quote #

Kit Request #

Project #

No. of Samples

Page of

Login

LIMS Ver

REMARKS	LAB 1 ID	LAB 2 ID

Sampled By & Title (Please sign and print name) — Date/Time

Received By (Please sign and print name) — Date/Time

Received By (Please sign and print name) — Date/Time

Received By (Please sign and print name) — Date/Time

Work Authorized By (Please sign and print name)

Relinquished By (Please sign and print name) — Date/Time

Relinquished By (Please sign and print name) — Date/Time

Relinquished By (Please sign and print name) — Date/Time

Shipped Via UPS BUS Fed-Ex Hand Other ____

Shipping #

Remarks

QC Level: 1 2 3 Other: ____

COC Rec	ICE
Ana Req	TEMP
Cust Seal	Ph

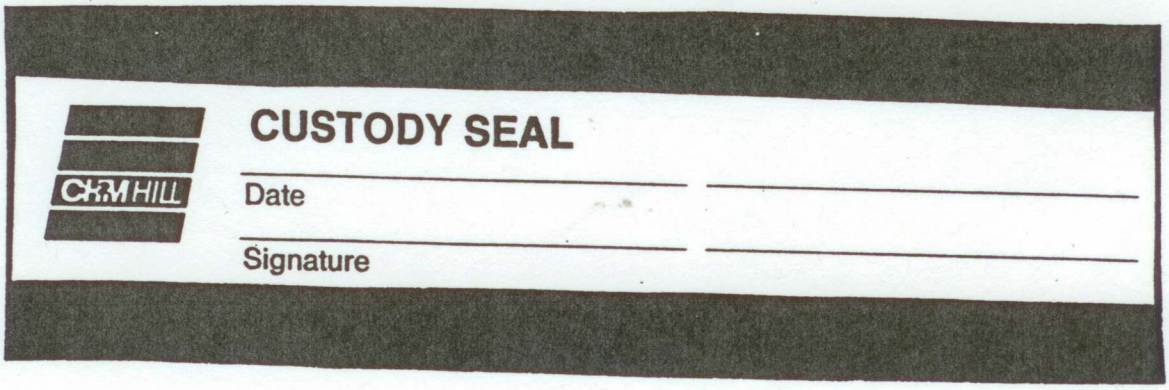
Instructions and Agreement Provisions on Reverse Side

DISTRIBUTION: Original - LAB, Yellow - LAB, Pink - Client

REV 3/94 FORM 340

Attachment C

Example Custody Seal


CRM HILL
CUSTODY SEAL
Date
Signature

STANDARD OPERATING PROCEDURE

Packaging and Shipping Procedures for Samples

I. Purpose and Scope

The purpose of this guideline is to describe the packaging and shipping of samples of various media to a laboratory for analysis.

II. Scope

The guideline only discusses the packaging and shipping of samples that are anticipated to have non-hazardous concentrations of chemical constituents. Whether or not samples should be classified as low-concentration or otherwise will depend upon the site history, observation of the samples in the field, odor, and photoionization-detector readings.

If the site is known to have produced high-concentration samples in the past or the sampler suspects that high concentrations of contaminants might be present in the samples, then the sampler should conservatively assume that the samples cannot be classified as low-concentration. Samples that are anticipated to have medium to high concentrations of constituents should be packaged and shipped accordingly.

If warranted, procedures for dangerous-goods shipping may be implemented. Dangerous goods and hazardous materials pose an unreasonable risk to health, safety, or property during transportation without special handling. As a result only employees who are trained under CH2M HILL Dangerous Goods Shipping course may ship or transport dangerous goods. Employees should utilize the HAZMAT ShipRight tool on the Virtual Office and/or contact a designated CH2M HILL HazMat advisor with questions.

III. Equipment and Materials

- Coolers
- Clear tape
- "This Side Up" labels
- "Fragile" labels
- Vermiculite
- Ziplock bags or bubble wrap
- Ice
- Chain-of-Custody form (completed)
- Custody seals

IV. Procedures and Guidelines

Low-Concentration Samples

A. Prepare coolers for shipment:

- Tape drains shut.
- Affix "This Side Up" labels on all four sides and "Fragile" labels on at least two sides of each cooler.
- Place mailing label with laboratory address on top of coolers.
- Fill bottom of coolers with about 3 inches of vermiculite or absorbent pads.

B. Arrange decontaminated sample containers in groups by sample number. Consolidate VOC samples into one cooler to minimize the need for trip blanks.

C. Affix appropriate adhesive sample labels to each container. Protect with clear label protection tape.

D. Seal each sample bottle within a separate ziplock plastic bag or bubble wrap, if available. Tape the bag around bottle. Sample label should be visible through the bag.

E. Arrange sample bottles in coolers so that they do not touch.

F. If ice is required to preserve the samples, cubes should be repackaged in zip-lock bags and placed on and around the containers.

G. Fill remaining spaces with vermiculite or absorbent pads.

H. Complete and sign chain-of-custody form (or obtain signature) and indicate the time and date it was relinquished to Federal Express or the courier.

J Close lid and latch.

K. Carefully peel custody seals from backings and place intact over lid openings (right front and left back). Cover seals with clear protection tape.

L. Tape cooler shut on both ends, making several complete revolutions with strapping tape. Cover custody seals with tape to avoid seals being able to be peeled from the cooler.

M. Relinquish to Federal Express or to a courier arranged with the laboratory. Place airbill receipt inside the mailing envelope and send to the sample documentation coordinator along with the other documentation.

Medium- and High-Concentration Samples:

Medium- and high-concentration samples are packaged using the same techniques used to package low-concentration samples, with potential additional restrictions. If applicable, the sample handler must refer to instructions associated with the shipping of dangerous goods for the necessary procedures for shipping by Federal Express or other overnight carrier. If warranted, procedures for dangerous-goods shipping may be implemented. Dangerous goods and hazardous materials pose an unreasonable risk to health, safety, or property during transportation without special handling. As a result only employees who are trained under CH2M HILL Dangerous Goods Shipping course may ship or transport dangerous goods. Employees should utilize the HAZMAT ShipRight tool on the Virtual Office and/or contact a designated CH2M HILL HazMat advisor with questions.

V. Attachments

None.

VI. Key Checks and Items

- Be sure laboratory address is correct on the mailing label
- Pack sample bottles carefully, with adequate vermiculite or other packaging and without allowing bottles to touch
- Be sure there is adequate ice
- Include chain-of-custody form
- Include custody seals

QAPP Worksheet #28: Analytical Quality Control and Corrective Action

Matrix: Aqueous

Analytical group: Volatile Organic Compounds

Analytical method/SOP: SW 846 8260B

TABLE 28-1

QC Sample	Number/Frequency	Method/SOP Acceptance Criteria	Corrective Action	Title/Position of Person Responsible for Corrective Action	Project-Specific MPC[a]
Tuning (Mass calibration check)	At beginning of run and every 12 hours	Meet all BFB criteria	Check instrument, reanalyze, re-tune	Lab personnel	Meet all BFB criteria
Method Blank (Lab Reagent Blank)	Prior to each analytical run	< RL (except acetone and methylene chloride)	Identify source and correct prior to continuing analysis	Lab personnel	< RL
Trip Blank (aqueous only)	One per shipment including aqueous VOCs	< RL	Identify source and correct	Field and/or laboratory personnel	< RL
Initial Calibration	Prior to sample analysis	RSD ≤ 15% of average RRF	Check instrument, recalibrate; qualify data	Lab personnel	RSD ≤15% of average RRF
Initial calibration check standard	After each initial calibration	RRF % D ≤ 20%	Recalibrate, qualify data	Lab personnel	RRF % D ≤ 20%
Continuing calibration check standard	Every 12 hours	RRF % D ≤ 20%	Recalibrate, qualify data	Lab personnel	RRF % D ≤ 20%
MS/MSD	1 per ≤ 20 samples	Mean recovery average 70-130 %R	Assume matrix bias; qualify data; note in case narrative	Lab personnel	Recovery 70-130% (each analyte); RPD ≤ 20%
LCS/LCSD	2 per batch of ≤ 20 samples	Average recovery 70–130% R; RPD ≤ 20%	Qualify data unless high recovery and/or not detected	Lab personnel	Average recovery 70–130% R; RPD ≤ 20%
Surrogate Compounds	all samples, standards, and blanks	70– 130% R	Reinject; qualify data	Lab personnel	70– 130% R
Internal Standards	all samples, standards, and blanks	-30 to +40% from initial/continuing calibration (for superfund program)	Check instruments, reanalyze affected samples if possible. If reanalysis not possible qualify data (except nondetects with high IS recovery).	Lab personnel	-30 to +40% from initial/continuing calibration

[a] Recovery and precision limits and measurement performance criteria are generic.

Matrix: Aqueous

Analytical group: Semivolatile Organic Compounds

Analytical method/SOP: SW 846 8270D

TABLE 28-2

QC Sample	Number/Frequency	Method/SOP Acceptance Criteria	Corrective Action	Title/Position of Person Responsible for Corrective Action	Project-Specific MPC[a]
Tuning (Mass calibration check)	At beginning of run and every 12 hours	Meet all DFTPP criteria	Check instrument, reanalyze, re-tune	Lab personnel	Meet all DFTPP criteria
Method Blank (Lab Reagent Blank)	Prior to each analytical run	< RL (except bis 2-ethylhexyl phthalate)	Identify source and correct prior to continuing analysis	Lab personnel	< RL
Initial Calibration	Prior to sample analysis	RSD ≤ 20% of average RRF	Check instrument, recalibrate; qualify data	Lab personnel	RSD ≤ 20% of average RRF
Initial calibration check standard	After each initial calibration	RRF % D ≤ 30%	Recalibrate, qualify data	Lab personnel	RRF % D ≤ 30%
Continuing calibration check standard	Every 12 hours	RRF % D ≤ 20%	Recalibrate, qualify data	Lab personnel	RRF % D ≤ 20%
MS/MSD	1 per ≤ 20 samples	70-130 %R	Assume matrix bias; qualify data; note in case narrative	Lab personnel	Recovery 70-130% (each analyte); RPD ≤ 20%
LCS/LCSD	2 per batch of ≤ 20 samples	70–130% R; RPD ≤ 20%	Qualify data unless high recovery and/or not detected	Lab personnel	70–130% R; RPD ≤ 20%
Surrogate Compounds	all samples, standards, and blanks	70–130% R	Reinject; qualify data	Lab personnel	70–130% R
Internal Standards	all samples, standards, and blanks	-30 to +40% from initial/continuing calibration (for superfund program)	Check instruments, reanalyze affected samples if possible. If reanalysis not possible qualify data (except nondetects with high IS recovery).	Lab personnel	-30 to +40% from initial/continuing calibration

[a] Recovery and precision limits and measurement performance criteria are generic.

Matrix: Aqueous

Analytical group: Metals

Analytical method/SOP: SW 846 6010C/SW6020A/SW7470AA

TABLE 28-3

QC Sample	Number/Frequency	Method/SOP Acceptance Criteria	Corrective Action	Title/Position of Person Responsible for Corrective Action	Project-Specific MPC[a]
Method Blank	1 per < 20 samples	all constituents < RL	Investigate source of contamination	Laboratory personnel	All constituents < RL
Initial Calibration Check	After each initial calibration	90–110% R	Reanalyze; qualify data	Laboratory personnel	90–110% R
Continuing Calibration Check (CCV)	1 per < 10 samples	90–110% R 80–120% R (SW7470A)	Reanalyze; qualify data	Laboratory personnel	90–110% R 80–120% R (SW7470A)
MS/MSD	1 per < 20 samples	80-120%R*	Qualify data	Laboratory personnel	80-120%R; RPD ≤ 20%
Low Level Check Std	Beginning and end of each analytical run	± 20 % of true value	Check instrument; recalibrate	Laboratory personnel	± 20 % of true value
Initial Calibration Blank (ICB)	After ICV	< RL	Investigate source of contamination	Laboratory personnel	< RL
Continuing Calibration Blank (CCB)	After every CCV	< RL	Investigate source of contamination	Laboratory personnel	< RL
Serial Dilution	Matrix spike sample	RPD < 20%	Qualify data	Laboratory personnel	RPD < 10%
Post Digestion Spike	Matrix spike sample	85-115%R	Qualify data	Laboratory personnel	85-115%R
Interference Check Sample (SW6010C and SW6020A only)	beginning, and end of each analytical run	< RL for all RCRA metals	As per SOP	Laboratory personnel	< RL
Laboratory Control Sample (LCS)/LCSD	2 per extraction batch of ≤ 20 samples	Average recovery 80-120%; RPD < 20%	Qualify data	Laboratory personnel	80-120% R; RPD ≤ 20%

[a] Recovery and precision limits and measurement performance criteria are generic.

QAPP Worksheet #29: Project Documents and Records

The electronic data will be used to generate validation reports, modeling results, data summary tables, maps, and other figures. This program will follow CH2M HILL standard procedures for environmental data collection.
Data collected during the field demonstrations will be reduced, reviewed, and a report on the findings will be tabulated in a standard format. The criteria used to identify and quantify the analytes will be those specified in the analytical methods. Data deliverables will be reported as "CLP-like" Sample Delivery Groups (SDGs). In addition, the USEPA shall have access to the lab and site data upon request.

The completed copies of the chain-of-custody records (both external and internal) accompanying each sample from time of initial bottle preparation to completion of analysis shall be attached to the analytical reports.

The Data Package will consist of SDGs in "PDF" format. The laboratory will upload the EDD directly to the project LocusFocus EIM database. The laboratory will provide the data package deliverables 21 business days after sample receipt of a complete sample delivery group. The Project Chemist (PC) will check the package to ensure all deliverables have been provided. If problems are identified, the laboratory will be alerted, and corrective actions will be requested. The data will be used to generate summary tables.

The electronic deliverable formats will be submitted according to the Honeywell EDD requirements. All deliverables must also undergo a QC check by the laboratory before delivery. The original data, tabulations, and electronic media are stored in a secure and retrievable fashion.

The Project Manager or Data Manager will maintain close contact with the PC to ensure all non-conformance issues are acted upon prior to data manipulation and assessment routines.

Data will be archived in project files and on electronic archive tapes for the duration of the project, 5 years, or as specified in contractual agreements.

The data flow from the laboratory and field to the project staff and data users will be sufficiently documented to ensure that data are properly tracked and reviewed before use.

In addition to the data management procedures, the laboratory will ensure that electronic and hardcopy records sufficient to recreate each analytical event are maintained. The minimum records the laboratory will keep contain the following:

- Raw data, including instrument printouts, bench work sheets, and/or chromatograms with compound identification and quantitation reports.
- Laboratory-specific written SOPs for each analytical method and QA/QC function in place at the time of analysis of project samples.
- Record keeping requirements for non-analytical data are included in the PDWP.

The below table lists field files and assessment reports that will be kept on file. Additional records will be kept on an as needed basis.

Sample Collection Documents and Records	On-site Analysis Documents and Records	Off-site Analysis Documents and Records	Data Assessment Documents and Records	Other
• Site and field logbooks • COC forms • Request forms and associated correspondence	• Field Analysis HACH Kits • Water quality parameters	• Internal COC forms • Sample preparation log • Standard traceability logs • Instrument calibration data • Instrument analysis logs • QC summary checklist with all relevant information • Sample analysis data • Instrument/computer printouts • Definition of qualifiers • Final report	• Sample acceptance checklist • Corrective action reports	• Telephone/email logs • Corrective action documentation • Equipment maintenance logs • Procurement request forms

QAPP Worksheets #31, #32, and #33: Assessments and Corrective Action

Assessments

Assessment Type	Responsible Party and Organization	Number/Frequency	Estimated Dates	Assessment Deliverable	Deliverable Due Date
Health and Safety Audit	Bill Berlett, Health and Safety Manager, CH2M HILL	Minimum of 1 per year	TBD	Audit checklist	TBD
QC Audit	Steve Martz/Kyle Block, Quality Control Manager, CH2M HILL	Minimum of 1 per year	TBD	Audit checklist	TBD
Laboratory Audit	Bernice Kidd, Project Chemist, CH2M HILL	As needed	Not applicable	Laboratory Audit Report	As needed

Assessment

Quality assurance audits may be performed by or under the direction of the project QM (Quality Manager). These audits will be implemented to evaluate the capability and performance of project and subcontractor personnel, items, activities, and documentation of the measurement system(s). The QM may plan, schedule, and approve system and performance audits based upon CH2M HILL SOP customized to the project requirements. At times, the QM may request additional personnel with specific expertise from company and/or project groups to assist in conducting performance audits. However, these personnel will not have responsibility for the project work associated with the performance audit.

System Audits

System audits, performed by the QM or designated auditors, will encompass a qualitative evaluation of measurement system components to ascertain their appropriate selection and application. In addition, field and laboratory quality control procedures and associated documentation may be system audited. These audits may be performed once during the performance of the project. However, if conditions adverse to quality are detected or if the Project Manager requests, additional audits may occur.

Performance Audits

The laboratory will be required to conduct an analysis of Performance Evaluation samples or provide proof that Performance Evaluation samples submitted by USEPA or a state agency have been analyzed within the past 12 months.

Formal Audits

Formal audits refer to any system or performance audit that is documented and implemented by the QM. These audits encompass documented activities performed by qualified lead auditors to a written procedure or checklists to objectively verify that quality assurance requirements have been developed, documented, and instituted in accordance with contractual and project criteria. Formal audits may be performed on project and subcontractor work at various locations.

Auditors who have performed the site audit after gathering and evaluating all data will write audit reports. Items, activities, and documents determined by lead auditors to be in noncompliance shall be identified at exit interviews conducted with the involved management. Noncompliance's will be logged and documented through audit findings, which are attached to and are a part of the integral audit report. These audit-finding forms are directed to management to satisfactorily resolve the noncompliance in a specified and timely manner.

The Project Manager has overall responsibility to ensure that all corrective actions necessary to resolve audit findings are acted upon promptly and satisfactorily. Audit reports must be submitted to the Project Manager within fifteen days of completion of the audit. Serious deficiencies will be reported to the Project Manager within 24 hours. All audit checklists; audit reports, audit findings, and acceptable resolutions are approved by the QM prior to issue. Verification of acceptable resolutions may be determined by re-audit or documented surveillance of the item or activity. Upon verification acceptance, the QM will close out the audit report and findings.

Assessment Response and Corrective Action

Assessment Type	Responsibility for Responding to Assessment Findings	Assessment Response Documentation	Timeframe for Response	Responsibility for Implementing Corrective Action	Responsible for Monitoring Corrective Action Implementation
Health and Safety Audit	Steve Zarlinski, PM CH2M HILL	Letter and any verification documentation	24 hours after notification	Field Team Leader, CH2M HILL	Bill Berlett, Health and Safety Manager CH2M HILL
QC Audit	Steve Zarlinski, PM CH2M HILL	Letter and any verification documentation	24 hours after notification	Field Team Leader, CH2M HILL	Steve Martz/Kyle Block, Quality Control Manager CH2M HILL

Corrective Action

The following procedures have been established to ensure that conditions adverse to quality, such as malfunctions, deficiencies, deviations, and errors, are promptly investigated, documented, evaluated, and corrected. Corrective action forms are included in the PDWP.

Procedure Description

When a significant condition adverse to quality is noted at site, laboratory, or subcontractor location, the cause of the condition will be determined and corrective action will be taken to preclude repetition. Condition identification, cause, reference documents, and corrective action planned to be taken will be documented and reported to the QM, Project Manager, Field Team Leader and involved subcontractor management, at a minimum. Implementation of corrective action is verified by documented follow-up action.

All project personnel have the responsibility, as part of the normal work duties, to promptly identify, solicit approved correction, and report conditions adverse to quality. Corrective actions will be initiated as follows:

- When predetermined acceptance standards are not attained;
- When procedure or data compiled are determined to be deficient;
- When equipment or instrumentation is found to be faulty;

- When samples and analytical test results are not clearly traceable;
- When quality assurance requirements have been violated;
- When designated approvals have been circumvented;
- As a result of system and performance audits;
- As a result of a management assessment;
- As a result of laboratory/field comparison studies; and
- As required by USEPA and USEPA SW-846 Methods.

Project management and staff, such as field investigation teams, remedial response planning personnel, and laboratory groups, monitor on-going work performance in the normal course of daily responsibilities. Work may be audited at the CH2M HILL office, sites, laboratories, or subcontractor locations. Activities or documents ascertained to be noncompliant with quality assurance requirements will be documented. Corrective actions will be mandated through audit finding sheets attached to the audit report. Audit findings are logged, maintained, and controlled by the Task Manager.

Personnel assigned to quality assurance functions will have the responsibility to issue and control Corrective Action Request (CAR) forms (See PDWP). The CAR identifies the out-of-compliance condition, reference document(s), and recommended corrective action(s) to be administered. The CAR is issued to the personnel responsible for the affected item or activity. A copy is also submitted to the Project Manager. The individual to whom the CAR is addressed returns the requested response promptly to the QA personnel, affixing his/her signature and date to the corrective action block, after stating the cause of the conditions and corrective action to be taken. The QA personnel maintain the log for status of CARs, confirms the adequacy of the intended corrective action, and verifies its implementation. CARs will be retained in the project file for the records.

Any project personnel may identify noncompliance issues; however, the designated QA personnel are responsible for documenting, numbering, logging, and verifying the close out action. The Project Manager will be responsible for ensuring that all recommended corrective actions are implemented, documented, and approved.

Reports to Management

CH2M HILL management personnel receive QA reports appropriate to their level of responsibility. The PM receives copies of all QA documentation. QC documentation is retained within the department that generated the product or service except where this documentation is a deliverable for a specific contract. QC documentation is also submitted to the QM for review and approval. Previous sections detailed the QA activities and the reports that they generate. A final audit report for each project may also be prepared. The reports may include:

- periodic assessment of measurement data accuracy, precision, and completeness;
- results of performance audits and/or system audits;
- significant QA problems and recommended solutions for future projects; and
- status of solutions to any problems previously identified.

Additionally, any incidents requiring corrective action will be fully documented.

QAPP Worksheet #34: Data Verification and Validation Inputs

Verification Input	Description	Internal/External	Responsible for Verification (Name, Organization)
Field Notes	Field notes will be reviewed internally and placed in the site file. A copy of the field notes will be attached to the final report.	Internal	FTL, CH2M HILL
COC and shipping forms	COC and shipping forms will be reviewed internally upon completion and verified against the packed coolers they represent. The shippers' signature on the COC should be initialed by the reviewer, a copy of the COC retained in the site file, and the original and remaining copies taped inside the cooler for shipment.	Internal	FTL, CH2M HILL
Audit Report	Upon report completion, a copy of all audit reports will be placed in the site file. If CAs are required, a copy of the documented CA taken will be attached to the appropriate audit report in the site file. At the beginning of each week and at the completion of the site work, site file audit reports will be reviewed internally to ensure that all appropriate CAs have been taken and that CA reports are attached. If CAs have not been taken, the Site Manager will be notified to ensure no action is taken.	Internal	Steve Zarlinski, PM, CH2M HILL
Laboratory Data	All laboratory data packages will be verified externally by the laboratory performing the work for completeness and technical accuracy prior to submittal.	External	Accutest (Marty Vitanza)

* Data for these specialty analyses will not be validated.

QAPP Worksheet #35: Data Verification Procedures

Step IIa/IIb	Validation Input	Description	Person(s) Responsible for Validation
IIa	Field SOPs	Verify that the sampling SOPs were followed	Mike Murphy, FTL, CH2M HILL
IIa	Analytical SOPs	Verify that the analytical SOPs were followed	Laboratory QA Officer/TBD Berney Kidd/CH2M HILL
IIa	Method QC Results	Verify that the required QC samples were run and met required limits	Laboratory QA Officer/TBD Berney Kidd/CH2M HILL
IIa/IIb	Data Validation	Validate 100 percent of the data to confirm quality	Berney Kidd/CH2M HILL
IIa/IIb	Data Usability Evaluation	Evaluate data based on precision, accuracy, representativeness, comparability and completeness for project objectives	Berney Kidd/CH2M HILL
IIb	Onsite Screening (such as PID readings)	Verify that the field data meets Work Plan requirements for completeness and accuracy based on field calibration records	Mike Murphy, FTL, CH2M HILL
IIb	Field Documentation	Verify accuarcy and completenss of field notes	Mike Murphy, FTL, CH2M HILL
IIb	Field QC Sample Results	Verify that the required field QC samples were run and met required limits	Laboratory QA Officer/TBD Berney Kidd/CH2M HILL

QAPP Worksheet #36: Data Validation Procedures

TABLE 36-1
Data Validation Procedures

Step IIa/IIb	Matrix	Analytical Group	Concentration Level	Validation Criteria	Data Validator (Title and Organizational Affiliation)
IIa/IIb	Groundwater	All methods	Low	Defined below	Berney Kidd/CH2M HILL Peeyush Gupta/HTS

Personnel involved in data validation will be independent of any data generation effort. The Project Chemist will be responsible for overseeing data validation. Data validation will be carried out when the data packages are received from the laboratory. It will be performed on an analytical batch basis using the summary results of calibration and laboratory quality control, as well as those of the associated field samples. Data packages will be reviewed for all constituents of concern. Raw data will be reviewed for approximately 10 percent of the data packages or as deemed necessary by the Project Chemist. Validation will be performed using the following procedures and those referenced for Level 3 or 4 as appropriate:

- A review of the data set narrative to identify any issues that the lab reported in the data deliverable
- A check of sample integrity (sample collection, preservation, and holding times)
- An evaluation of basic QC measurements used to assess the accuracy, precision, and representativeness of data, including QC blanks, LCSs, MS/MSDs, surrogate recovery when applicable, and field or laboratory duplicate results
- A review of sample results, target compound lists, and detection limits to verify that project analytical requirements are met
- Initiation of corrective actions, as necessary, based on the data review findings
- Qualification of the data using appropriate qualifier flags, as necessary, to reflect data usability limitations

Level 3 validation procedures will also include reviewing the evaluation of calibration and quality control summary results against the project requirements and other method-specific QC requirements.

Data validation will be patterned after EPA guidelines for organic and inorganic data review, substituting the calibration and quality control requirements specified in this QAPP for those specified in the guidelines. The flagging criteria in Tables 36-2 and 36-3 will be used. The qualifier flags are defined in Table 36-4.

Qualifier flags, if required, will be applied to the electronic sample results. If multiple flags are required for a result, the most severe flag will be applied to the electronic result. The hierarchy of flags from the most severe to the least severe will be as follows: R, UJ, U, and J.

Any significant data quality problems will be brought to the attention of the Project Chemist.

TABLE 36-2
Flagging Conventions for Organic Methods
Quanta, Quality Assurance Project Plan

Quality Control Check	Evaluation	Flag	Samples Affected
Holding Time	Holding time exceed for extraction or analysis by less than a factor of two	J positive results UJ non-detects	affected samples
	Holding time exceed for extraction or analysis by a factor of two	J positive results R non-detects	affected samples
Temperature	temperature exceedance >6°C if received within 24 hr	UJ non-detects	affected samples
	temperature exceedance >6°C if received > 24 hr	UJ non-detects, J positive results	
Sample Preservation (volatiles)	Sample preservation requirements not met and analyzed out of holding time if preservation not performed in the field, but performed in the laboratory upon receipt, no flagging is required	J positive results R non-detects	affected samples
Sample Integrity (volatiles)	Professional Judgment on sample condition Example: Bubbles in VOA vial used for analysis	J positive results/professional judgment R non-detects/professional judgment	affected samples
GC/MS Instrument Performance Check	Mass assignment in error and laboratory cannot reprocess data	R all results	all samples in batch
	Ion abundance criteria not met	R all results if critical ions involved, use judgment otherwise	all samples in batch
Initial Calibration	%RSD > criteria in WS#28 or R <0.990	J positive results UJ non-detects	analyte in associated samples
	%RSD exceeds criteria by more than a factor of 2	J positive results R non-detects	analyte in associated samples
Continuing Calibration Verification (ICV and CCV)	% difference or % drift > criteria in WS#28	J positive results	analyte in associated samples
	% difference or % drift < criteria in WS#28	J positive results UJ non-detects	analyte in associated samples

TABLE 36-2
Flagging Conventions for Organic Methods
Quanta, Quality Assurance Project Plan

Quality Control Check	Evaluation	Flag	Samples Affected
Laboratory Control Sample (LCS)/Laboratory Control Sample Duplicate (CLSD)	%R > criteria in WS#28	J positive results	analyte in associated samples
	%R < criteria in WS#28 but ≥10%	J positive results UJ non-detects	analyte in associated samples
	%R < criteria in WS#28 but <10%	J positive results R non-detects	analyte in associated samples
	RPD > criteria in WS#28	J positive results	analyte in associated samples
Method Blank	Multiply highest blank value by 5 (by 10 for common lab contaminants, acetone, methylene chloride, MIBK, cyclohexane, phthalates)	U positive results <5 x highest blank concentration (<10 x for common contaminants)	all associated samples in batch
Equipment Blank	Multiply highest blank value by 5 (by 10 for common lab contaminants, acetone, methylene chloride, MIBK, cyclohexane, phthalates)	U positive results <5 x highest blank concentration (<10 x for common contaminants)	all associated samples in batch
Trip Blank	Multiply highest blank value by 5 (by 10 for common lab contaminants, acetone, methylene chloride, MIBK, cyclohexane, phthalates)	U positive results <5 x highest blank concentration (<10 x for common contaminants)	all associated samples in batch
Matrix Spike/Matrix Spike Dup (MS/MSD) does not apply if sample result is greater than four times the spike value	%R > criteria in WS#28	J positive results	parent sample
	%R < criteria in WS#28 but ≥10%	J positive results UJ non-detects	parent sample
	%R < criteria in WS#28 but <10%	J positive results R non-detects	parent sample
	RPD > criteria in WS#28	J positive results	parent sample
Surrogates	%R > criteria in WS#28	J positive results	parent sample
	%R < criteria in WS#28 but ≥10%	J positive results UJ non-detects	parent sample
	%R < criteria in WS#28 but <10%	J positive results R non-detects	parent sample

TABLE 36-2
Flagging Conventions for Organic Methods
Quanta, Quality Assurance Project Plan

Quality Control Check	Evaluation	Flag	Samples Affected
Laboratory Duplicates	Both sample results >5 times RL and RPD>UCL	J positive results	laboratory duplicate pair
	One or both samples <5 times RL and a difference between results of ± 2 times RL	J positive results UJ non detects	laboratory duplicate pair
Field Duplicates	Both sample results >5 times RL and RPD>30%	J positive results	field duplicate pair
	One or both samples <5 times RL and a difference between results of ± 2 times RL	J positive results UJ non-detects	field duplicate pair

Initial calibration should be based on average response factors or a linear regression equation. Laboratories will need Project Chemist approval to use a nonlinear calibration curve.

TABLE 36-3
Flagging Conventions for Inorganic Methods
Quanta, Quality Assurance Project Plan

Quality Control Check	Evaluation	Flag	Samples Affected
Holding Time	Holding time exceeded for digestion or analysis	J positive results	affected samples
	Holding time exceeded for digestion or analysis by a factor of two	J positive results for all analytes R non-detects for all analytes	affected samples
Temperature (does not apply to SW6010C or SW6020)	temperature exceedance >6°C if received within 24 hr	UJ non-detects	affected samples
	temperature exceedance >6°C if received > 24 hr	UJ non-detects, J positive results	affected samples
Sample preservation	Sample preservation requirements not met. If preservation not performed in the field, but performed in the laboratory upon receipt, no flagging is required	J positive results for all analytes R non-detects for all analytes	affected samples
Initial Calibration	Correlation coefficient $\leq$0.995 or %RSD < criteria in WS#28	J positive results UJ non-detects	analyte in associated samples
Initial Calibration Verification (ICV)	%R > criteria in WS#28	J positive results	analyte in associated samples
	%R < criteria in WS#28	J positive results UJ non-detects	analyte in associated samples
Continuing Calibration Verification (CCV)	%R > criteria in WS#28	J positive results	analyte in associated samples
	%R < criteria in WS#28	J positive results UJ non-detects	analyte in associated samples
Interference Check Sample (metals only)	%R > criteria in WS#28	J positive results	analyte in associated samples
	%R < criteria in WS#28	J positive results UJ non-detects	analyte in associated samples

TABLE 36-3
Flagging Conventions for Inorganic Methods
Quanta, Quality Assurance Project Plan

Quality Control Check	Evaluation	Flag	Samples Affected
Laboratory Control Sample (LCS)/Laboratory Control Sample Duplicate (LCSD)	%R > criteria in WS#28	J positive results	analyte in associated samples
	%R < criteria in WS#28 but ≥10%	J positive results UJ non-detects	analyte in associated samples
	%R < criteria in WS#28 but <10%	J positive results R non-detects	analyte in associated samples
	RPD > criteria in WS#28	J positive results	analyte in associated samples
Calibration Blank (ICB or CCB)	Multiply highest blank value by 5	U positive results < 5 x highest blank concentration	all associated samples in batch
	If negative blank and absolute value is greater than the MDL and negative value is >25% of sample result	J positive results UJ non-detects	analyte in associated samples
Method Blank	Multiply highest blank value by 5	U positive results < 5 x highest blank concentration	all associated samples in batch
	If negative blank and absolute value is greater than the MDL and negative value is >25% of sample result	J positive results UJ non-detects	analyte in associated samples
Equipment Blank	Multiply highest blank value by 5	U positive results < 5 x highest blank concentration	all associated samples in batch
Matrix Spike/Matrix Spike Dup (MS/MSD) does not apply if sample result is greater than four times the spike value	%R > criteria in WS#28	J positive results	parent sample
	%R < criteria in WS#28 but ≥10%	J positive results UJ non-detects	parent sample
	%R < criteria in WS#28 but <10%	J positive results R non-detects	parent sample
	RPD > criteria in WS#28	J positive results	parent sample
Serial Dilution (metals only)	If concentration is >50 times the MDL and % difference is > 10%	J positive results	parent sample

TABLE 36-3
Flagging Conventions for Inorganic Methods
Quanta, Quality Assurance Project Plan

Quality Control Check	Evaluation	Flag	Samples Affected
Post-Digestion Spike metals only perform if dilution test fails	%R > criteria in WS#28	J positive results	parent sample
	%R < criteria in WS#28 but ≥10%	J positive results UJ non-detects	parent sample
	%R < criteria in WS#28 but <10%	J positive results R non-detects	parent sample
Laboratory Duplicates (if no MSD or LCSD performed)	Both sample results >5 times RL and RPD>UCL	J positive results	parent sample
	One or both samples <5 times RL and a difference between results of ± 2 times RL	J positive results UJ non-detects	parent sample
Field Duplicates	Both sample results >5 times RL and RPD>30%	J positive results	field duplicate pair
	One or both samples <5 times RL and a difference between results of ± 2 times RL	J positive results UJ non-detects	field duplicate pair

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TABLE 36-4
Qualifier Flag Definitions
Quanta, Quality Assurance Project Plan

Flag	Definition
J	The result is an estimated quantity. The associated numerical value is the approximate concentration of the analyte in the sample.
R	The data are unusable. The sample results are rejected due to serious deficiencies in meeting Quality Control (QC) criteria. The analyte may or may not be present in the sample.
U	This analyte was analyzed for but not detected at the specified detection limit.
UJ	The analyte was analyzed for, but was not detected. The reported quantitation limit is approximate and may be inaccurate or imprecise.
NJ	The analysis indicates the presence of an analyte that has been “tentatively identified” and the associated numerical value represents its approximate concentration.

QAPP Worksheet #37: Data Usability Assessment

The data usability assessment is an evaluation based on the results of data verification and validation in the context of the overall project decisions or objectives. The assessment determines whether the project execution and resulting data meet the project DQOs. Both the sampling and analytical activities must be considered, with the ultimate goal of assessing whether the final, qualified results support the decisions to be made with the data.

All the results will be assembled and statistically reported for an overall Data Quality Evaluation, which will be provided as an appendix to the Remedial Design Report. The assessment report will identify precision and accuracy exceedances with respect to the laboratory performance for each batch of samples, as well as comparability of field and lab duplicates. Discussion will cover precision, accuracy, representativeness, comparability, and completeness as detailed in Worksheet #12 and detailed below.

Precision

Laboratory precision is measured by the variability associated with duplicate (two) or replicate (more than two) analyses. One type of sample that can be used to assess laboratory precision is the LCS. Multiple LCS analyses over the duration of the project can be used to evaluate the overall laboratory precision for the project. In this case, the comparison is not between a sample and a duplicate sample analyzed in the same batch, but between LCSs analyzed in multiple batches.

Total precision is the measurement of the variability associated with the entire sampling and analytical process. It is determined by analysis of duplicate field samples and measures variability introduced by both the laboratory and field operations. Field duplicate samples and MSD samples shall be analyzed to assess field and laboratory precision. For duplicate sample results, the precision is evaluated using the relative percent difference (RPD). For replicate results, the precision is measured using the relative standard deviation (RSD). The formula for the calculation of RPD and PRD are provided below.

If calculated from duplicate measurements:

$$RPD = \frac{(C_1 - C_2)\ x\,100\%}{(C_1 + C_2)/2} \qquad (1)$$

Where:

RPD = relative percent difference

C_1 = larger of the two observed values

C_2 = smaller of the two observed values

If calculated from three or more replicates, use RSD rather than RPD:

$$RSD = (s/\bar{y})\ x\,100\% \quad (2)$$

Where:

RSD = relative standard deviation

s = standard deviation

$\bar{y}$ = mean of replicate analyses

Standard deviation, s, is defined as follows:

$$S = \sqrt{\sum_{i=1}^{n} \frac{(yi - \bar{y})^2}{n-1}} \qquad (3)$$

Where:

S = standard deviation

yi = measured value of the ith replicate

$\bar{y}$ = mean of replicate analyses

n = number of replicates

Accuracy

Accuracy reflects the total error associated with a measurement. A measurement is considered accurate when the reported value agrees with the true value or known concentration of the spike or standard within acceptable limits. Analytical accuracy is measured by comparing the percent recovery of analytes spiked into an LCS to a control limit. For many methods of organic compound analysis, surrogate compound recoveries are also used to assess accuracy and method performance for each sample analyzed.

Both accuracy and precision are calculated for each analytical batch, and the associated sample results are interpreted by considering these specific measurements. The formula for calculation of accuracy is included in below as percent recovery (%R) from pure and sample matrices.

For measurements where matrix spikes are used:

$$\%R = 100\% \; x \left[\frac{S-U}{C_{sa}} \right] \qquad (4)$$

Where:

%R = percent recovery

S = measured concentration in spiked aliquot

U = measured concentration in unspiked aliquot

Csa = actual concentration of spike added

For situations where a standard reference material (SRM) is used instead of or in addition to matrix spikes:

$$\%R = 100\% \; x \left[\frac{C_m}{C_{sm}} \right] \quad (5)$$

Where:

%R = percent recovery

Cm = measured concentration of SRM

Csm = actual concentration of SRM

Representativeness

Representativeness is a qualitative term that refers to the degree in which data accurately and precisely depicts the characteristics of a population, whether referring to the distribution of contaminant within a sample, a sample within a matrix, or the distribution of a contaminant at a site. Representativeness is determined by appropriate program design, with consideration of elements such as proper well locations, drilling and installation procedures, operations process locations, and sampling locations. Objectives for representativeness are defined for each sampling and analysis task and are a function of the investigative objectives. Assessment of representativeness shall be achieved through use of the standard field, sampling, and analytical procedures.

Comparability

Comparability is a qualitative indicator of the confidence with which one data set can be compared to another data set. The objective for this QA/QC program is to produce data with the greatest possible degree of comparability. The number of matrices that are sampled and the range of field conditions encountered are considered in determining comparability. Comparability is achieved by using standard methods for sampling and analysis, reporting data in standard units, normalizing results to standard conditions, and using standard and comprehensive reporting formats. Complete field documentation using standardized data collection forms shall support the assessment of comparability. Historic comparability shall be achieved through consistent use of methods and documentation procedures throughout the project. Assessment of comparability is primarily subjective and results should be interpreted by experienced environmental professionals with a clear knowledge of the DQOs and project decisions.

Completeness

Completeness is a measure of the amount of valid data obtained compared with the amount that was expected to be obtained under correct, normal conditions. It is calculated for the aggregation of data for each analyte measured for any particular sampling event or other defined set of samples (for example, by site) as set out in the DQOs. Valid data are data which are usable in the context of the project goals. Completeness is calculated and reported for each method, matrix, and analyte combination. The number of valid results divided by the number of possible individual analyte results, expressed as a percentage, determines the completeness of the data set. For completeness requirements, valid results are all results not qualified with an R-flag after a

usability assessment has been performed. Completeness should not be determined only on the basis of laboratory data qualifiers. The goal for completeness is 95 percent.

Defined as follows for all measurements:

$$\%C = 100\% \; x\left[\frac{V}{T}\right] \qquad (6)$$

Where:

%C = percent completeness
V = number of measurements judged valid
T = total number of measurements

.

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Attachment 1

U.S. ENVIRONMENTAL PROTECTION AGENCY
REGION II

GROUND WATER SAMPLING PROCEDURE
LOW STRESS (Low Flow) PURGING AND SAMPLING

I. SCOPE & APPLICATION

This Low Stress (or Low-Flow) Purging and Sampling Procedure is the EPA Region II standard method for collecting low stress (low flow) ground water samples from monitoring wells. Low stress Purging and Sampling results in collection of ground water samples from monitoring wells that are representative of ground water conditions in the geological formation. This is accomplished by minimizing stress on the geological formation and minimizing disturbance of sediment that has collected in the well. The procedure applies to monitoring wells that have an inner casing with a diameter of 2.0 inches or greater, and maximum screened intervals of ten feet unless multiple intervals are sampled. The procedure is appropriate for collection of ground water samples that will be analyzed for volatile and semi-volatile organic compounds (VOCs and SVOCs), pesticides, polychlorinated biphenyls (PCBs), metals, and microbiological and other contaminants in association with all EPA programs.

This procedure does not address the collection of light or dense non-aqueous phase liquids (LNAPL or DNAPL) samples, and should be used for aqueous samples only. For sampling NAPLs, the reader is referred to the following EPA publications: DNAPL Site Evaluation (Cohen & Mercer, 1993) and the RCRA Ground-Water Monitoring: Draft Technical Guidance (EPA/530-R-93-001), and references therein.

II. METHOD SUMMARY

The purpose of the low stress purging and sampling procedure is to collect ground water samples from monitoring wells that are representative of ground water conditions in the geological formation. This is accomplished by setting the intake velocity of the sampling pump to a flow rate that limits drawdown inside the well casing.

Sampling at the prescribed (low) flow rate has three primary benefits. First, it minimizes disturbance of sediment in the bottom of the well, thereby producing a sample with low turbidity (i.e., low concentration of suspended particles). Typically, this saves time and analytical costs by eliminating the need for collecting and analyzing an additional filtered sample from the same well. Second, this procedure

minimizes aeration of the ground water during sample collection, which improves the sample quality for VOC analysis. Third, in most cases the procedure significantly reduces the volume of ground water purged from a well and the costs associated with its proper treatment and disposal.

III. ADDRESSING POTENTIAL PROBLEMS

Problems that may be encountered using this technique include a) difficulty in sampling wells with insufficient yield; b) failure of one or more key indicator parameters to stabilize; c) cascading of water and/or formation of air bubbles in the tubing; and d) cross-contamination between wells.

Insufficient Yield

Wells with insufficient yield (i.e., low recharge rate of the well) may dewater during purging. Care should be taken to avoid loss of pressure in the tubing line due to dewatering of the well below the level of the pump's intake. Purging should be interrupted before the water level in the well drops below the top of the pump, as this may induce cascading of the sand pack. Pumping the well dry should therefore be avoided to the extent possible in all cases. Sampling should commence as soon as the volume in the well has recovered sufficiently to allow collection of samples. Alternatively, ground water samples may be obtained with techniques designed for the unsaturated zone, such as lysimeters.

Failure to Stabilize Key Indicator Parameters

If one or more key indicator parameters fails to stabilize after 4 hours, one of three options should be considered: a) continue purging in an attempt to achieve stabilization; b) discontinue purging, do not collect samples, and document attempts to reach stabilization in the log book; c) discontinue purging, collect samples, and document attempts to reach stabilization in the log book; or d) Secure the well, purge and collect samples the next day (preferred). The key indicator parameter for samples to be analyzed for VOCs is dissolved oxygen. The key indicator parameter for all other samples is turbidity.

Cascading

To prevent cascading and/or air bubble formation in the tubing, care should be taken to ensure that the flow rate is sufficient to maintain pump suction. Minimize the length and diameter of tubing (i.e., 1/4

or 3/8 inch ID) to ensure that the tubing remains filled with ground water during sampling.

Cross-Contamination

To prevent cross-contamination between wells, it is strongly recommended that dedicated, in-place pumps be used. As an alternative, the potential for cross-contamination can be reduced by performing the more thorough "daily" decontamination procedures between sampling of each well in addition to the start of each sampling day (see Section VII, below).

Equipment Failure

Adequate equipment should be on-hand so that equipment failures do not adversely impact sampling activities.

IV. PLANNING DOCUMENTATION AND EQUIPMENT

- Approved site-specific Field Sampling Plan/Quality Assurance Project Plan (QAPP). This plan must specify the type of pump and other equipment to be used. The QAPP must also specify the depth to which the pump intake should be lowered in each well. Generally, the target depth will correspond to the mid-point of the most permeable zone in the screened interval. Borehole geologic and geophysical logs can be used to help select the most permeable zone. However, in some cases, other criteria may be used to select the target depth for the pump intake. In all cases, the target depth must be approved by the EPA hydrogeologist or EPA project scientist.

- Well construction data, location map, field data from last sampling event.

- Polyethylene sheeting.

- Flame Ionization Detector (FID) and Photo Ionization Detector (PID).

- Adjustable rate, positive displacement ground water sampling pump (e.g., centrifugal or bladder pumps constructed of stainless steel or Teflon). A peristaltic pump may only be used for inorganic sample collection.

- Interface probe or equivalent device for determining the presence or absence of NAPL.

- Teflon or Teflon-lined polyethylene tubing to collect samples for organic analysis. Teflon or Teflon-lined polyethylene, PVC, Tygon or polyethylene tubing to collect samples for inorganic analysis. Sufficient tubing of the appropriate material must be available so that each well has dedicated tubing.

- Water level measuring device, minimum 0.01 foot accuracy, (electronic preferred for tracking water level drawdown during all pumping operations).

- Flow measurement supplies (e.g., graduated cylinder and stop watch or in-line flow meter).

- Power source (generator, nitrogen tank, etc.).
- Monitoring instruments for indicator parameters. Eh and dissolved oxygen must be monitored in-line using an instrument with a continuous readout display. Specific conductance, pH, and temperature may be monitored either in-line or using separate probes. A nephalometer is used to measure turbidity.

- Decontamination supplies (see Section VII, below).

- Logbook (see Section VIII, below).

- Sample bottles.

- Sample preservation supplies (as required by the analytical methods).

- Sample tags or labels, chain of custody.

V. SAMPLING PROCEDURES

Pre-Sampling Activities

1. Start at the well known or believed to have the least contaminated ground water and proceed systematically to the well with the most contaminated ground water. Check the well, the lock, and the locking cap for damage or evidence of tampering. Record observations.

2. Lay out sheet of polyethylene for placement of monitoring and sampling equipment.

3. Measure VOCs at the rim of the unopened well with a PID and FID instrument and record the reading in the field log book.

4. Remove well cap.

5. Measure VOCs at the rim of the opened well with a PID and an FID instrument and record the reading in the field log book.

6. If the well casing does not have a reference point (usually a V-cut or indelible mark in the well casing), make one. Note that the reference point should be surveyed for correction of ground water elevations to the mean geodesic datum (MSL).

7. Measure and record the depth to water (to 0.01 ft) in all wells to be sampled prior to purging. Care should be taken to minimize disturbance in the water column and dislodging of any particulate matter attached to the sides or settled at the bottom of the well.

8. If desired, measure and record the depth of any NAPLs using an interface probe. Care should be taken to minimize disturbance of any sediment that has accumulated at the bottom of the well. Record the observations in the log book. If LNAPLs and/or DNAPLs are detected, install the pump at this time, as described in step 9, below. Allow the well to sit for several days between the measurement or sampling of any DNAPLs and the low-stress purging and sampling of the ground water.

Sampling Procedures

9. Install Pump: Slowly lower the pump, safety cable, tubing and electrical lines into the well to the depth specified for that well in the EPA-approved QAPP or a depth otherwise approved by the EPA hydrogeologist or EPA project scientist. The pump intake must be kept at least two (2) feet above the bottom of the well to prevent disturbance and resuspension of any sediment or NAPL present in the bottom of the well. Record the depth to which the pump is lowered.

10. Measure Water Level: Before starting the pump, measure the water level again with the pump in the well. Leave the water level measuring device in the well.

11. Purge Well: Start pumping the well at 200 to 500 milliliters per minute (ml/min). The water level should be monitored approximately every five minutes. Ideally, a steady flow rate should be maintained that results in a stabilized water

level (drawdown of 0.3 ft or less). Pumping rates should, if needed, be reduced to the minimum capabilities of the pump to ensure stabilization of the water level. As noted above, care should be taken to maintain pump suction and to avoid entrainment of air in the tubing. Record each adjustment made to the pumping rate and the water level measured immediately after each adjustment.

12. Monitor Indicator Parameters: During purging of the well, monitor and record the field indicator parameters (turbidity, temperature, specific conductance, pH, Eh, and DO) approximately every five minutes. The well is considered stabilized and ready for sample collection when the indicator parameters have stabilized for three consecutive readings as follows (Puls and Barcelona, 1996):

    ±0.1 for pH
    ±3% for specific conductance (conductivity)
    ±10 mv for redox potential
    ±10% for DO and turbidity

    Dissolved oxygen and turbidity usually require the longest time to achieve stabilization. The pump must not be removed from the well between purging and sampling.

13. Collect Samples: Collect samples at a flow rate between 100 and 250 ml/min and such that drawdown of the water level within the well does not exceed the maximum allowable drawdown of 0.3 ft. VOC samples must be collected first and directly into sample containers. All sample containers should be filled with minimal turbulence by allowing the ground water to flow from the tubing gently down the inside of the container.

    Ground water samples to be analyzed for volatile organic compounds (VOCs) require pH adjustment. The appropriate EPA Program Guidance should be consulted to determine whether pH adjustment is necessary. If pH adjustment is necessary for VOC sample preservation, the amount of acid to be added to each sample vial prior to sampling should be determined, drop by drop, on a separate and equal volume of water (e.g., 40 ml). Ground water purged from the well prior to sampling can be used for this purpose.

14. Remove Pump and Tubing: After collection of the samples, the tubing, unless permanently installed, must be properly discarded or dedicated to the well for resampling by hanging the tubing inside the well.

15. Measure and record well depth.

16. Close and lock the well.

VI. FIELD QUALITY CONTROL SAMPLES

Quality control samples must be collected to determine if sample collection and handling procedures have adversely affected the quality of the ground water samples. The appropriate EPA Program Guidance should be consulted in preparing the field QC sample requirements of the site-specific QAPP.

All field quality control samples must be prepared exactly as regular investigation samples with regard to sample volume, containers, and preservation. The following quality control samples should be collected during the sampling event:

- Field duplicates
- Trip blanks for VOCs only
- Equipment blank (not necessary if equipment is dedicated to the well)

As noted above, ground water samples should be collected systematically from wells with the lowest level of contamination through to wells with highest level of contamination. The equipment blank should be collected after sampling from the most contaminated well.

VII. DECONTAMINATION

Non-disposable sampling equipment, including the pump and support cable and electrical wires which contact the sample, must be decontaminated thoroughly each day before use ("daily decon") and after each well is sampled ("between-well decon"). Dedicated, in-place pumps and tubing must be thoroughly decontaminated using "daily decon" procedures (see #17, below) prior to their initial use. For centrifugal pumps, it is strongly recommended that non-disposable sampling equipment, including the pump and support cable and electrical wires in contact with the sample, be decontaminated thoroughly each day before use ("daily decon").

EPA's field experience indicates that the life of centrifugal pumps may be extended by removing entrained grit. This also permits inspection and replacement of the cooling water in centrifugal pumps. All non-dedicated sampling equipment (pumps, tubing, etc.) must be

decontaminated after each well is sampled ("between-well decon," see #18 below).

17. **Daily Decon**

A) Pre-rinse: Operate pump in a deep basin containing 8 to 10 gallons of potable water for 5 minutes and flush other equipment with potable water for 5 minutes.

B) Wash: Operate pump in a deep basin containing 8 to 10 gallons of a non-phosphate detergent solution, such as Alconox, for 5 minutes and flush other equipment with fresh detergent solution for 5 minutes. Use the detergent sparingly.

C) Rinse: Operate pump in a deep basin of potable water for 5 minutes and flush other equipment with potable water for 5 minutes.

D) Disassemble pump.

E) Wash pump parts: Place the disassembled parts of the pump into a deep basin containing 8 to 10 gallons of non-phosphate detergent solution. Scrub all pump parts with a test tube brush.

F) Rinse pump parts with potable water.

G) Rinse the following pump parts with distilled/ deionized water: inlet screen, the shaft, the suction interconnector, the motor lead assembly, and the stator housing.

H) Place impeller assembly in a large glass beaker and rinse with 1% nitric acid (HNO_3).

I) Rinse impeller assembly with potable water.

J) Place impeller assembly in a large glass bleaker and rinse with isopropanol.

K) Rinse impeller assembly with distilled/deionized water.

18. **Between-Well Decon**

A) Pre-rinse: Operate pump in a deep basin containing 8 to 10 gallons of potable water for 5 minutes and flush other equipment with potable water for 5 minutes.
B) Wash: Operate pump in a deep basin containing 8 to 10 gallons of a non-phosphate detergent solution, such as Alconox, for 5

minutes and flush other equipment with fresh detergent solution for 5 minutes. Use the detergent sparingly.

C) Rinse: Operate pump in a deep basin of potable water for 5 minutes and flush other equipment with potable water for 5 minutes.

D) Final Rinse: Operate pump in a deep basin of distilled/deionized water to pump out 1 to 2 gallons of this final rinse water.

VIII. FIELD LOG BOOK

A field log book must be kept each time ground water monitoring activities are conducted in the field. The field log book should document the following:

- Well identification number and physical condition.
- Well depth, and measurement technique.
- Static water level depth, date, time, and measurement technique.
- Presence and thickness of immiscible liquid layers and detection method.
- Collection method for immiscible liquid layers.
- Pumping rate, drawdown, indicator parameters values, and clock time, at three to five minute intervals; calculate or measure total volume pumped.
- Well sampling sequence and time of sample collection.
- Types of sample bottles used and sample identification numbers.
- Preservatives used.
- Parameters requested for analysis.
- Field observations of sampling event.
- Name of sample collector(s).
- Weather conditions.
- QA/QC data for field instruments.

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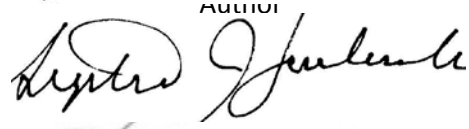
Equipment Decontamination
July 16, 2012
Erik Spande/CH2M HILL

APPROVED:

Author 7/16/2012
Date



7/16/2012
Date

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Date

Annual Review Summary

Annual Reviewer	Erik Spande			
Date of Review	6/7/2013			

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Attachments

A. Purpose and Applicability

The purpose of this Standard Operating Procedure (SOP) is to establish uniform procedures for equipment decontamination. The procedures outlined in this SOP are applicable the decontamination of heavy equipment, drilling equipment, well materials, and sampling equipment.

B. Summary of Method

Decontamination procedures were established in Section 3.2 of the Field Sampling Plan by Parsons (2005), and these instructions are summarized in this SOP.

C. Definitions

AHA Activity Hazard Analysis

FSP Field Sampling Plan

FTL Field Team Leader

HandS health and safety database

OSHA Occupational Safety and Health Administration

SSC Site Safety Coordinator

USEPA United States Environmental Protection Agency

D. Health and Safety

CH2M HILL staff will have current Occupational Safety and Health Administration (OSHA) and 8-hour OSHA refresher training, as applicable. Staff will review and sign the site health and safety plan (HASP), will review and sign the activity hazard analysis (AHA) for the task, and understand and use personal protective equipment as specified in the HASP.

E. Personnel Qualifications

This SOP is written for CH2M HILL staff. The field team leader (FTL) will be responsible for the execution of the Work Plan and Field Sampling Plan. The FTL will be identified by the Project Manager before the start of the task. The site safety coordinator (SSC) will have completed the CH2M HILL-required SSC training and will be responsible for the execution of the HASP. All CH2M HILL staff will have current OSHA and 8-hour OSHA refresher training, as applicable. The SSC will verify that all HASP-required training using the HandS database and any lapsed training is updated before the start of the task, and that copies of training for each staff member are onsite.

F. Equipment and Supplies

Attachment 1 contains equipment and supplies for decontamination activities.

G. Procedural Steps

Decontamination Pad for Drilling Equipment or Other Heavy Equipment

- The location of the decontamination pad will be determined in the field.

- The drilling or heavy equipment subcontractor will construct a decontamination pad of high-density polyethylene sheeting.
- The pad will be sloped such that water drains toward a sump, and the sides of the decontamination pad will be bermed to contain decontamination water.
- Water from the sump will be pumped to a 55-gallon drum.

Heavy Equipment Decontamination

- The subcontractor will use a high-pressure steam-cleaning unit for decontamination of drill rigs, augers, bits, rods, tools, split-spoon samplers, and tremie pipes before work and after the conclusion of each boring.
- Wire brushes will be used to remove dirt, grease, and oil as needed.
- Tools, drill rods, and augers will be placed on sawhorses or polyethylene plastic sheets following steam cleaning. Direct contact with the ground will be prevented.
- Well material such as well casings and screens will be decontaminated as heavy equipment unless they arrive at the site in factory-sealed plastic sleeves.

Sampling Equipment Decontamination

- Dedicated and disposable equipment will not need to be decontaminated. All sampling equipment that will be reused will be decontaminated using these procedures. Sampling equipment such as split spoons may be steam-cleaned (see Heavy Equipment Decontamination) or may be decontaminated by using the procedure noted below.
- Clean disposable equipment (groundwater sampling tubing, bladders for pumps, sampling spoons, etc.) should be used when necessary to minimize cross-contamination. Disposable equipment does not have to be decontaminated.
- Conduct sampling equipment decontamination at the decontamination pad. If the pad is not present, then sampling equipment decontamination will occur within buckets that are placed on plastic sheeting.
- Wash sampling equipment such as low-flow pumps, bowls, spoons, augers, Geoprobe rods, and Macrocore samplers with potable water and then phosphate-free detergent (such as Alconox).
- Equipment will undergo a acid rinse consisting of a 10 percent solution of reagent grade nitric acid and deionized water if sampling for metals.
- Rinse with potable water and then rinse with distilled water.
- Between rinses, place equipment on plastic sheeting or aluminum foil, as needed.
- Decontaminated equipment will be wrapped in aluminum foil for storage or transportation from the decontamination area to the sampling area. Decontaminated equipment will not be placed on the ground.

H. Data and Records Management

Record the time and procedures used for decontamination in the field book or field form. Field data will be finalized the day of collection. Hardcopy records will be scanned and copied to a project directory at least weekly. Electronic records will be backed up on a laptop or similar device daily, and will be copied to a project directory at least weekly.

I. Quality Assurance and Quality Control

Follow and document procedures noted above and in accordance with quality assurance/quality control (QA/QC) procedures specified in the QAPP, as previously amended (CH2M HILL, 2005, 2006, 2008), and in the current QAPP Addendum (CH2M HILL, 2012).

J. References

CH2M HILL. 2005. Quality Assurance Project Plan (Revised), Operable Unit 1, Quanta Resources OU1, Edgewater, New Jersey. October.

CH2M HILL. 2006. Quality Assurance Project Plan (Revised), Operable Unit 1, Quanta Resources OU1, Edgewater, New Jersey. November.

CH2M HILL. 2008. Quality Assurance Project Plan (Revised), Operable Unit 1, Quanta Resources OU1, Edgewater, New Jersey. November.

CH2M HILL. 2012a. Draft Predesign Investigation Work Plan, Quanta Resources Corporation Superfund Site, Operable Unit 1, Edgewater, New Jersey. May.

CH2M HILL. 2012b. Field Sampling Plan for Predesign Investigation, Operable Unit 1, Quanta Resources OU1, Edgewater, New Jersey. May.

Parsons. 2005. *Field Sampling Plan, Operable Unit 1, Quanta Resources OU1,* Edgewater, New Jersey. May.

K. Attachments/Checklists

1. Equipment Checklist

Attachment 1 – Equipment List

Heavy equipment and well material decontamination equipment will be supplied by the drilling subcontractor.

- Plastic-lined decontamination pad of high density polyethylene sheeting—sides of decon pad will be bermed
- Sump for decontamination pad
- High-pressure steam cleaning unit
- Sawhorses
- Polyethylene plastic sheets
- 55-gallon drums for decon water

Decontamination Equipment for Sampling Equipment and PPE

- Alconox® solution (or equivalent)
- Potable water
- Deionized water
- Diluted reagent grade acid (Nitric Acid)
- Spray bottles for alconox solution, diluted acid, potable water, and distilled water. Each type of spray bottle used for decontamination will be labeled.
- Brushes
- 5-gallon buckets with lids
- Four or more 5-gallon buckets for decontamination of pumps
- Aluminum foil
- Protective gloves (nitrile or latex, per HASP)

Attachment 2

ACCUTEST LABORATORIES
STANDARD OPERATING PROCEDURE

Lab Manager: Wendy Mc

QA Manager: [signature]

Effective Date: 9/25/13

TITLE: COLD VAPOR ANALYSIS OF MERCURY FOR WATER SAMPLES

REFERENCE: EPA 245.1, revision 3.0 (1994) and SW846 7470A (modified)

Revised Sections: ***11.8, 12.10.1, 12.12.***

1.0 SCOPE AND APPLICATION

1.1 This method can be applied for the analysis of mercury for all potable and non-potable water samples. This SOP is based on the May 1994 revision of EPA method 245.1. The reporting limit for mercury water samples based on the procedures outlined in this SOP, is 0.0002 mg/l.

1.2 Aqueous wastewater may also be analyzed following method 7470A. The modification to this method are a direct scale-down of the reagents and the use of an automated analyzer.

2.0 SUMMARY

2.1 Cold vapor mercury is a flameless AA procedure based on the absorption of radiation at 253.7 by mercury vapor. Organic mercury compounds are oxidized and the mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Results are quantitated by comparison to a daily calibration curve.

3.0 REPORTING LIMIT AND METHOD DETECTION LIMIT

3.1 Reporting Limit. The reporting limit for this method is established at the lowest concentration standard in the calibration curve. Detected concentrations below this concentration cannot be reported without qualification.

3.2 Method Detection Limit. Experimentally determine MDLs using the procedure specified in 40 CFR, Part 136, Appendix B. This value represents the lowest reportable concentration of an individual compound that meets the method qualitative identification criteria.

3.2.1 Experimental MDLs must be determined annually for this method.

3.2.2 Process all raw data for the replicate analysis in each MDL study.

4.0 DEFINITIONS

BATCH: A group of samples which behave similarly with respect to the sampling or the

testing procedures being employed and which are processed as a unit. For QC purposes, if the number of samples in a group is greater than 20, then each group of 20 samples or less will all be handled as a separate batch.

CALIBRATION CHECK STANDARD. The calibration check standard is a mid-range calibration standard. The calibration check standard must be run at a frequency of 10 percent or less. The mid-level calibration check standard criteria is either ± 10 percent of the true value.

EXTERNAL CHECK STANDARD. The external check standard is a standard from a separate source than the calibration curve that is used to verify the accuracy of the calibration standards. An external check must be run a minimum of once per quarter for all analyses where a check is commercially available. The laboratory should initially assess laboratory performance of a check standard using the control limits generated by the external check supplier. In house limits should also be generated once sufficient external check standard data is available to generate limits (usually a minimum of 20 to 30 analyses). If the external check is outside of the control limits for a given parameter, all samples must be reanalyzed for that parameter after the problem has been resolved.

SPIKE BLANK OR LAB CONTROL SAMPLE. Digest and analyze a laboratory control sample or spike blank with each set of samples. A minimum of one lab control sample or spike blank is required for every 20 samples. Assess laboratory performance against the control limits specified in the SOP. In house limits should also be generated once sufficient external check standard data is available to generate limits (usually a minimum of 20 to 30 analyses). If the lab control is outside of the control limits for a parameter, all samples must be redigested or redistilled and reanalyzed for that parameter. The exception is if the lab control recovery is high and the results of the samples to be reported are less than the reporting limit. In that case, the sample results can be reported with no flag.

MATRIX: The component or substrate (e.g., water, soil) which contains the analyte of interest.

MATRIX DUPLICATE: A duplicate sample is digested at a minimum of 1 in 20 samples. The relative percent difference (RPD) between the duplicate and the sample should be assessed. The duplicate RPD is calculated as shown below. Assess laboratory performance against the control limits that are specified in the SOP. In house limits are generated once sufficient duplicate data is available to generate limits (usually a minimum of 20 to 30 analyses). If a duplicate is out of control, flag the results with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of ± the reporting limit, then the duplicate is considered to be in control. Note: If control limits are not specified in the SOP, use default limits of ± 20% RPD.

$$\frac{(|\text{Sample Result} - \text{Duplicate Result}|) \times 100}{(\text{Sample Result} + \text{Duplicate Result})/2} = \text{Duplicate RPD}$$

MATRIX SPIKE: The laboratory must add a known amount of each analyte to a minimum of 1 in 10 samples. The matrix spike recovery is calculated as shown below. Assess laboratory performance against the control limits that are specified in the SOP. In house limits are generated once sufficient matrix spike data is available to generate limits (usually a minimum of 20 to 30 analyses). If a matrix spike is out of control, then the results should

be flagged with the appropriate footnote. If the matrix spike amount is less than one fourth of the sample amount, then the sample cannot be assessed against the control limits and should be footnoted to that effect.

$$\frac{\text{(Spiked Sample Result - Sample Result)}}{\text{(Amount Spiked)}} \times 100 = \text{Matrix Spike Recovery}$$

MATRIX SPIKE DUPLICATES: Intralaboratory split samples spiked with identical concentrations of target analyte(s). The spiking occurs prior to sample preparation and analysis. They are used to document the precision and bias of a method in a given sample matrix.

$$\frac{(|\text{MS Result - MSD Result}|) \times 100}{\text{(MS Result + MSD Result)/2}} = \text{MSD RPD}$$

METHOD BLANK. The laboratory must digest and analyze a method blank with each set of samples. A minimum of one method blank is required for every 20 samples. For a running batch, a new method blank is required for each different digestion day. If no digestion step is required, then the method blank is equivalent to the reagent blank. The method blank must contain the parameter of interest at levels of less that the reporting limit for that parameter. If the method blank contains levels over the reporting limits, the samples must be redigested or redistilled and reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the method blank level. In addition, if all the samples are less than a client required limit and the method blank is also less than that limit, then the results can be reported as less than that limit.

METHOD DETECTION LIMITS (MDLS). The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte. MDLs should be determined approximately once per year for frequently analyzed parameters.

REAGENT BLANK: The reagent blank is a blank that has the same matrix as the samples, i.e., all added reagents, but did not go through sample preparation procedures. The reagent blank is an indicator for contamination introduced during the analytical procedure. (Note: for methods requiring no preparation step, the reagent blank is equivalent to the method blank.) Either a reagent blank or a method blank must be analyzed with each batch of 20 samples or less. The concentration of the analyte of interest in the reagent blank must be less than the reporting limit for that analyte. If the reagent blank contains levels over the reporting limits, the samples must be reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the reagent blank level. In addition, if all the samples are less than a client required limit and the reagent blank is also less than that limit, then the results can be reported as less than that limit.

REAGENT GRADE: Analytical reagent (AR) grade, ACS reagent grade, and reagent grade are synonymous terms for reagents which conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.

REAGENT WATER: Water that has been generated by any method which would achieve the performance specifications for ASTM Type II water. For organic analyses, see the

definition of organic-free reagent water.

REFERENCE MATERIAL: A material containing known quantities of target analytes in solution or in a homogeneous matrix. It is used to document the bias of the analytical process.

STANDARD CURVE: A plot of concentrations of known analyte standards versus the instrument response to the analyte. Calibration standards are prepared by successively diluting a standard solution to produce working standards which cover the working range of the instrument. Standards should be prepared at the frequency specified in the appropriate section. The calibration standards should be prepared using the same type of acid or solvent and at the same concentration as will result in the samples following sample preparation. This is applicable to organic and inorganic chemical analyses.

5.0 HEALTH & SAFETY

5.1 The analyst must follow normal safety procedures as outlined in the Accutest Laboratory Safety Manual which includes the use of safety glasses and lab coats. In addition, all acids are corrosive and must be handled with care. Flush spills with plenty of water. If acids contact any part of the body, flush with water and contact the supervisor.

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical must be treated as a potential health hazard. Exposure to these reagents should be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets must be made available to all personnel involved in these analyses.

5.3 After the mercury digestate is reduced to Hg vapor, it must be handled in a closed system or in a hood to prevent inhalation of the toxic vapor. Make sure that the Hg instrument is vented directly to a hood.

6.0 PRESERVATION AND HOLDING TIME

6.1 All water samples must be preserved by acidification with nitric acid to a pH of 2 or lower and stored in a polyethylene or glass container.

6.2 All samples must be analyzed within 28 days of the date of collection.

7.0 INTERFERENCES

7.1 Possible interference from sulfide is eliminated by the addition of potassium permanganate. Concentrations of sulfide as sodium sulfide as high as 20 mg/l do not interfere with mercury recoveries when following this method. High copper concentrations (> 10 mg/l) may also interfere with mercury recoveries.

7.2 Samples that are high in chloride such as seawater, brine, and industrial effluent may require as much as 25 ml of additional permanganate. NOTE: When chloride

concentrations are high, hydroxylamine sulfate and stannous sulfate should be used in place of the corresponding chlorides.

7.3 Finally, certain volatile organic materials will also absorb at this wavelength and can interfere. It can be determined if this type of interference is present by doing a preliminary run without reagents.

8.0 APPARATUS

8.1 Three Leeman instruments are available for analysis. **They are Leeman Hydra II** automated analyzers. Refer to the instrument manuals for further details on this instrumentation, including proper venting and safety requirements. Instrument maintenance is outlined below.

8.1.1 Change the sample tubing as needed.

8.1.2 Change the drying tubing as needed.

8.1.3 Clean the exterior of the instrument as needed.

8.1.4 Adjust the Hg lamp as needed. This can be done in the software on both instruments.

8.1.5 Complete any other maintenance required to maintain the instrument in good running order including, but not limited to, cleaning the cell, changing other tubing, changing the Hg lamp, etc.

8.2 Heating Equipment.

8.2.1 Graphite heating block. Capable of heating at 95 °C for 2 hours.

8.3 Digestion Bottles. Disposable plastic digestion tubes are used with the graphite heating block.

8.3.1 Disposable plastic digestion tubes (65 ml volume) with tops for graphite heating block.

8.4 Class A, to deliver, volumetric cylinders for measuring initial sample volumes and for calibrating glass tubes as outlined above.

8.5 Automatic pipettor bottles. Refer to EQA063 for calibration information.

9.0 REAGENTS

All chemicals listed below are reagent grade unless otherwise specified. Deionized water should be used whenever water is required. All solutions listed below may be scaled up or down proportionally as needed.

9.1 Sulfuric acid, concentrated.

9.2 Nitric acid, concentrated. This acid must have a low mercury content.

9.3 Dilution acid. To approximately 400 ml of DI water, add 33.4 ml of concentrated sulfuric and 16.6 ml of concentrated nitric. Dilute to a final volume of 1000 ml. This dilution acid is used for making dilutions of digested samples.

9.4 Stannous chloride. Add 25 ml of concentrated hydrochloric acid to approximately 400 ml of DI water. Dilute to 500 ml with DI water and mix well. Add 50 g of stannous chloride dihydrate or 42 g of stannous chloride anhydrous and dissolve. Make sure that this solution is dissolved while in use.

9.4.1 Stannous sulfate may be used in place of stannous chloride.

9.5 Sodium chloride-Hydroxylamine hydrochloride. Add 240 g of sodium chloride and 240 g of hydroxylamine hydrochloride to 2000 ml of water. Mix well. Hydroxylamine sulfate may be used in place of hydroxylamine hydrochloride.

9.6 Potassium Permanganate, 5 percent solution, w/v. Add 50 g of potassium permanganate to 1000 ml of water and mix well. **Caution** - Potassium permanganate is a strong oxidizing agent. Handle with care.

9.7 Potassium Persulfate, 5 percent solution, w/v. Dissolve 50.0 g of potassium persulfate in 1000 ml of water and mix well. **Caution** - Potassium persulfate is a strong oxidizing agent. Handle with care.

9.8 Mercury standard solutions.

9.8.1 10 ppm Hg solution. Using a 1.00 ml volumetric pipet or autopipet, add 1.00 ml of 1000 ppm stock (to be purchased from a vendor such as Fisher) to a 100 ml volumetric flask containing approximately 75 ml of water and 2.0 ml of concentrated nitric acid. Dilute to volume with water and mix well. This standard may be held for up to 28 days.

9.8.1.1 The 10 ppm external source should be made up following the directions in 9.8.1.

9.8.2 **30.0** ppb Hg solution. Using an autopipet, add **0.300** ml of 10 ppm Hg solution to a 100 ml volumetric flask containing approximately 75 ml of water and 2.0 ml of concentrated nitric acid. Dilute to volume with deionized water and mix well. This standard must be made fresh daily.

9.8.2.1 The 30.0 ppb external source should be made up following the directions in 9.8.2.

9.8.3 **3** ppb Hg solution. Using volumetric pipets or autopipets, add 10.0 ml of **30.0** ppb Hg solution to a 100 ml volumetric flask containing approximately 75 ml of DI water and 2.0 ml of concentrated nitric acid. Dilute to volume with deionized water and mix well. This standard must be made fresh daily.

10.0 WATER DIGESTION FOR GRAPHITE HEATING BLOCK

Below is a step-by-step procedure for the digestion and analysis of water samples for mercury.

10.1 If necessary, acid rinse disposable digestion tubes with 10% nitric acid and deionized water before use.

10.2 Make up a standard curve consisting of 5 standards and a blank. Suggested concentrations are shown below. All standards are made up to a final volume of **30** ml. Different concentrations may also be used, as long as all of the method requirements are met. Make sure to clearly label each bottle. Calibration standards must be prepared fresh with each digestion batch.

ml of 3 ppb Hg solution	**ml of 30 ppb Hg solution**	**Ml of DI water**	**Total ug of Hg**	**ug/L of Hg**
0.000	0.000	**30**	0.000	0.000
2.00	0.000	**28.0**	**0.006**	0.20
5.00	0.000	**25.0**	**0.015**	0.50
0.00	1.00	**29.0**	**0.030**	1.00
0.00	2.50	**27.5**	**0.075**	2.50
0.00	5.00	**25.0**	**0.150**	5.00

10.3 Samples. For each sample, homogenize the sample well and pour out a representative aliquot of the sample into the digestion tube to the 30 ml mark. The digestion tubes are purchased from independent vendor and they are certified for the 50ml only. Accutest calibrates the 30ml volume for the 10% of the total tubes of any lot. The calibration results must be recorded in a log book with a QC/QA controlled book number. A smaller volume may be used if there are matrix problems or high levels of mercury in the sample using a class A, to deliver, graduated cylinder.

10.4 Make up additional quality control samples as shown below, using a final volume of **30** ml for each check standard. (Note: if a different standard curve is run, then the levels of the CCV and ICV standards should be adjusted accordingly in accordance with the requirements in the methods) Make sure to clearly label each bottle. Make sure to prepare enough CCV checks for the entire run. The ICV check must be from an alternate source of standards than the calibration curve. The CCV must be made from the same source as the calibration curve. A low check standard at the level of the CRDL (0.20 ug/l) is also required. This 0.20 ug/l check can be made up as outlined for the standard curve.

Sample ID	**ml of** 30 **ppb Hg solution**	**ml of DI water**	**Total ug of Hg**
CCV Check(s)	2.5	27.5	**0.075**
MB	0.0	30	**0.0**
MS	2.0	(a)	**0.06 (b)**
MSD	2.0	(a)	**0.06 (b)**
ICV	3.0	**27.0**	**0.09**
LCS	2.0	**28.0**	**0.06**

(a) **30** ml of sample
(b) plus the level of Hg in the sample.

10.5 To all samples, QC, and standards add the reagents listed below, swirling the samples well after each addition of reagent. Allow the samples to stand for at least 15 minutes after the addition of the permanganate. If the sample decolorizes, add additional permanganate until the purple color persists.

- **1.5** ml of conc. sulfuric acid.
- **0.75** ml of conc. nitric acid.
- **4.0** ml of 5% permanganate solution.

Wait 15 minutes, then

- **2.4** ml of potassium persulfate solution.

10.5.1 All of the additions shown can be done with a bottle pipettor which must be accurate to within a range of 90 to 110%.

10.6 Cap the samples and place them in the graphite heating block and heat for 2 hours at **90 to** 95 °C. Record the digestion times and temperature.

10.7 Enter the prep data into the LIMS system, double checking all volumes and spike amounts. After the prep data is checked, it can be approved and is available for use in the final calculations.

11.0 COLD VAPOR ANALYSIS PROCEDURE HYDRA II

11.1 While the samples are digesting, begin setting up the Leeman analyzer following the steps outlined below. Additional instructions are available in the instrument operators' manual.

11.1.1 Turn on the nitrogen and adjust to 60 to 90 psi. Turn on the instrument power if it is not already on.

11.1.2 Check the pump tubing and make sure that it is not flattened. Change if appropriate. Put the tubing in the clamps on the pump. Check the drying line and make sure that it is clean. Put fresh stannous chloride solution in the stannous chloride bottle. Fill the rinse bath or rinse bottle with fresh 10% nitric acid. The bath should be filled no more than ¾ full. Place the autosampler line and the stannous chloride line in the rinse container.

11.1.3 Turn on the analyzer and allow it to warm up.

11.1.3.1 For the Hydra AA II, open the Envoy software. Go to Method and click Instrument Control. On the Instrument Control page, click the startup icon. This will turn on the lamp, gas, and pump. You may also turn on/off the lamp, gas and pump individually on the Instrument Control Page.

11.1.4 Tighten the pump clamps until the flow is coming evenly through the lines. Do not overtighten.

11.1.4.1 Go to the Instrument control tab and pick the gas control test option. The input should be approximately 0.25 LPM. If the pressures are not correct, check with the area supervisor or manager before proceeding.

11.1.5 Start a batch to save your data.

11.1.5.1 Create a new chapter (Data File) by clicking Analysis. The batch should normally be named H5 followed by the month date and year, followed by the matrix designation for the batch, following by the run number. For example, the first water batch on instrument for 3/24/03 would be named H5032411w1. The realtime print option can also be turned on from this tab.

11.1.5.2 Set up autosampler racks containing the samples that are going to be run.

11.1.5.3 Create a new sequence by clicking sequence-new. Type the sequence name. After typing the samples in to sequence page make sure to click update and save. CCV and CCB checks can be entered in the macro column of the sequence page.

11.1.6 Set up the calibration.

11.1.6.1 Go to the Method menu, enter or verify the standard concentration by clicking on the standard tab. Also select number of replicates to be run for each standard. Normally one replicate is run per standard. The check standard concentrations and acceptance ranges are also defined under this standard info tab. Make sure to always click apply when any changes are made in a tab.

11.2 Add hydroxylamine hydrochloride to all samples and standards as outlined below.

12.2.1 Add **1.8** ml of hydroxylamine hydrochloride solution to each standard and sample and swirl until the solution has been completely decolorized. Transfer to a calibrated glass cylinder and dilute to a final volume of **50** ml and swirl to mix.

12.2.2 They hydroxylamine hydrochloride can be added using a bottle pipettor which is accurate in a range of 90 to 110%.

11.3 Measure out aliquots of the digested standards and samples into the autosampler cups. Work from the prep log and double check all transfers. Let all samples sit uncovered in the open autosampler vials for a minimum of one minute. Place the racks in the autosampler. Move the stannous chloride line into the stannous chloride bottle.

11.4 Start the calibration.

12.4.1 Click run sequence. The instrument will run the calibration and then pause. Click stop. Go to the Calibration page. Accept the calibration and then print the calibration. Click the Document icon, then choose HG5-PDF. Rename the file as MA*****_cal.

11.5 After the calibration has been accepted, start to run the samples.

12.5.1 For the Hydra AA II, go to the Sequence page. Right click on the first sample (ie. ICV) and click start from here.

11.6 Review the data. Any samples that are over the range of the curve should be diluted with the dilution acid (see Section 9.3) and reanalyzed. It is recommended that any sample analyzed after a sample with a value over the curve be reanalyzed for confirmation. Make sure to bracket every 10 samples with CCV and CCB checks.

11.7 Both paper and electronic reports can be generated using the report option. Never delete any samples from the reports. Electronic reports should be transferred into the LIMS system where the final calculations are done.

12.7.1 Go to analysis-Click result-Click chapter. Then go to report and select report spec. The normal report spec is "ACCUTEST". Click OK. Click on chapter in order to select all samples. Then click report output and then csv.file. Save as MA*****.csv. To print, select printer output and then type the report title (i.e. MA*****) and enter OK.

11.8 The calculations are done in the LIMS as described below. A final volume of 30.0 ml is used for calculation purposes for graphite heating block digestions. (The volume of 50.0 ml is factored out since all standards and samples are brought up to the same final volume and standard concentrations are calculated based on 30.0 ml.)

Final sample concentration in mg/L =

$$\frac{\text{concentration in the digestate in ug/l x final volume in ml}}{\text{Initial volume in ml}}$$

11.9 Review the data in the LIMS, adding comments and accepting results as appropriate.

11.10 Shut down the instruments.

12.10.2 To shut down the Hydra AA II, move the stannous chloride line from the stannous chloride bottle to the 10% HNO3 rinse bottle. Let the system rinse with 10% HNO3 for several minutes. Then switch the line to DI water bottle and let rinse for several more minutes. Let the pump and gas run until the lines are completely dry. Then go to instrument control menu and click off icon for Lamp, Gas and Pump.

12.0 QUALITY CONTROL

Below is a summary of the quality control requirements for this method. Make sure to check with the laboratory supervisor or manager for any additional client specific quality control requirements.

12.1 Instrument Detection Limits (IDLs). The instrument detection limits must be done a minimum of once per year or when instrument conditions change significantly. The IDL is generated by running 10 replicates of a digested blank. The IDL is then defined as 3 times the standard deviation of the 10 replicates of the blank.

12.2 Method Detection Limits (MDLs). MDLs should be established using a solution spiked at approximately 3 times the estimated detection limit. To determine the MDL values, take seven replicate aliquots of the spiked sample and process through the entire analytical method. The MDL is calculated by multiplying the standard deviation of the replicate analyses by 3.143, which is the student's t value for a 99% confidence level. MDLs should be determined approximately once per year or whenever there is a significant change in the background or instrument response.

12.3 Instrument Calibration. The instrument must be calibrated daily or at a minimum of once every 24 hours and each time the instrument is set up. Calibration standards should be prepared fresh with each preparation batch. A minimum of a blank and 5 standards are required. The correlation coefficient of the curve must be a minimum of 0.995. No samples should be analyzed until all of the calibration criteria are met. Resloping is acceptable as long as it is immediately preceded and immediately followed by a complaint CCV and CCB.

12.4 Linear Dynamic Range (LDR). For each instrument, the upper limit of the linear dynamic range must be established. A linear calibration should be prepared from 3 standards, one of which is close to the upper limit of the linear range. The LDR is determined by analyzing succeedingly higher standard concentrations of mercury until the observed analyte concentration is no more than 10 percent below the true value of the standard. Sample concentrations that are greater than 90% of the determined upper LDR limit must be analyzed using dilutions. The LDR should be verified annually or whenever there is a significant change in the instruments analytical performance.

12.5 Quality Control Sample (also referred to as Initial Calibration Verification Standard (ICV)). At a minimum of once per quarter, a standard from a different source than the calibration standard must be analyzed. Normally this is analyzed at the beginning of the run after the CCV and CCB checks. The ICV must be within 10 percent of the true value. It is recommended that this standard be analyzed with each run so that it is included with all client reports. For SW846 7470A, this standard should be at a concentration near the midpoint of the calibration curve. If the ICV is outside of the acceptance limits, then the problem must be corrected and the ICV reanalyzed and shown to be within QC limits before any samples can be reported. All reported samples must be bracketed by an ICV which meets acceptance criteria.

12.5.1 If the ICV is biased high and all sample results are < RL, then, at the discretion of the data reviewer, data may be reported.

12.6 Method Blank. The laboratory must digest and analyze a method blank with each set of samples. A minimum of one method blank is required for every 20 samples. For a running batch, a new method blank is required for each different digestion day. The method blank must contain mercury at less that the reporting limit. If the method blank contains over that limit, the samples must be redigested or reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the method blank level. In addition, if all the samples are less than a client required limit and the method blank is also less than that limit, then the results can be reported as less than that limit.

12.7 Lab Control Sample. The laboratory must digest and analyze a laboratory control sample (spike blank) with each set of samples. A minimum of one lab control sample is required for every 20 samples. For a running batch, a new lab control sample is required for each different digestion day. For method 245.1, the laboratory must assess laboratory performance of an aqueous lab control against recovery limits of 85 to 115 percent. For method 7470A, the laboratory must assess laboratory performance of an aqueous lab control against recovery limits of 80 to 120 percent. In either case, if the lab control recovery is high and the results of the samples to be reported are less than the reporting limit, then the sample results can be reported with no flag. If the lab control recovery is low or there are samples above the reporting limit, then all affected samples must be redigested and reanalyzed.

12.8 Matrix Spike.

12.8.1 For method 245.1, the laboratory must add a known amount of each analyte to a minimum of 1 in 10 samples. The spike recovery should be within the limits of 70 to 130. If a matrix spike is out of control, then the results should be flagged with the appropriate footnote. If the matrix spike amount is less than one fourth of the sample amount, then the sample cannot be assessed against the control limits and should be footnoted to that effect.

12.8.2 For method 7470A, the laboratory must add a known amount of each analyte to a minimum of 1 in 20 samples. The laboratory should assess the matrix spike recovery against limits of 75 to 125. (In house control limits are also generated on an annual basis and are used to support the default limits.) An exception to this rule occurs where the sample concentration exceeds the spike concentration by a factor of 4 or more. If the matrix spike fails this criterion, then the sample should be flagged as showing possible matrix interferences.

12.8.3 Both the matrix spike amount and the sample amount are calculated to the IDL for any given element. Any value less than the IDL is treated as zero. Refer to the calculation shown below.

$$\frac{\text{(Spiked Sample Result - Sample Result)}}{\text{(Amount Spiked)}} \times 100 = \text{MS Recovery}$$

12.9 Matrix Spike Duplicate or Matrix Duplicate. The laboratory must digest a matrix spike duplicate or a duplicate sample for a minimum of 1 in 20 samples. Matrix spike

duplicates are normally used unless otherwise specified by client requirements. The relative percent difference (rpd) between the matrix spike duplicate and the matrix spike or between the duplicate and the sample should be assessed. The calculations for both rpds are shown below.

12.9.1 For method 245.1, the control limits for the matrix spike duplicates or the duplicates are calculated on an annual basis and are used to assess whether a matrix spike duplicate or a duplicate is in control. If it is out of control, then the results should be flagged with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of $\pm$ the reporting limit, then the duplicate is considered to be in control.

12.9.2 For method 7470A, the duplicate or matrix spike duplicate RPD must be assessed against a limit of 20% RPD. (In house control limits are also generated on an annual basis and are used to support the default limits.) If it is out of control, then the results should be flagged with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of $\pm$ the reporting limit, then the duplicate is considered to be in control.

12.9.3 Both the duplicate amount and the sample amount are calculated to the IDL for any given element. Any value less than the IDL is treated as zero. Refer to the calculations shown below.

$$\frac{(\text{Sample Result} - \text{Duplicate Result}) \times 100}{(\text{Sample Result} + \text{Duplicate Result}) \times 0.5} = \%\ \text{RPD}$$

or

$$\frac{(|\text{MS Result} - \text{MSD Result}|) \times 100}{(\text{MS Result} + \text{MSD Result})/2} = \text{MSD RPD}$$

12.10 Continuing Calibration Verification. (Also known as the instrument performance check solution.) The CCV must be from the same source as the calibration curve.

12.10.1 Analyze the continuing calibration verification solution and the continuing calibration blank after every tenth sample and at the end of the sample run. If the CCV solution is not within a method specified range of the true value, then no samples can be reported in the area bracketed by that CCV. (Note: the exception is if the CCV is biased high and the samples are less than the detection limit. In that case, the samples can be reported with no flag.) The CCV concentration should be at or near the mid-range of the calibration curve.

12.10.1.1 For methods 245.1 and 7470A, the CCV must be within 10 percent of the true value.

12.10.2 The ICCV check must also be analyzed at the beginning of the run, immediately after the instrument is calibrated. For method 245.1, this first

check must be within 5 percent of the true value. If it is not and there is not a problem with the standard solution, the instrument should be recalibrated and rechecked.

13.10.2.1 This check is not required for method SW846 7470A.

12.11 Continuing Calibration Blank. Analyze the continuing calibration verification solution and the continuing calibration blank after every tenth sample and at the end of the sample run. If the CCB is not less than the reporting limit, then no samples can be reported in the area bracketed by the failing CCB.

12.12 CRA (Low) Check. For all runs, a low check at the level of the CRDL (0.20 ug/l) or reporting limit must be analyzed at the beginning of the run before analyzing any samples, but not before the ICV. No specific acceptance criteria are listed in any of the methods for this standard at this time. The method criteria of 70-130% recovery is applied to this low check standard. If this criterion is not met, then all samples associated with this CRA check must be reanalyzed along with a compliant CRA check.

12.12.1 If the CRA is biased high and there is no mercury found in the samples, then the sample results may be reported for mercury. If the CRA is biased high and there is mercury found in the samples, then the samples with Hg at levels ranging from the CCV to the high standard may be reported. Samples with levels of mercury between the CRA and the CCV standard may be biased high and cannot be reported.

12.12.2 Some client may require additional bracketing low checks to be analyzed. Client specific limits may also be required. Check with the area supervisor or manager for more information.

13.0 DOCUMENTATION REQUIREMENTS

Refer to the laboratory Quality Assurance Manual for additional documentation requirements.

13.1 Sample Worksheets. Digestion data sheets for the Hg water samples must show all digestion information including the sample ID's, sample volumes, bottle numbers, start times, end times, and pressure or temperature, as appropriate for all digestions. The digestion method (i.e digestion block) must be indicated on the digestion sheet. All sample information should be clearly entered on these sheets. In addition, any unusual characteristics of the samples or the digestion procedure should be noted in the Comments sections. Make sure also that all dilutions are clearly documented.

13.2 Standards and Reagents. All stocks and reagents must be recorded in the reagent logbook. All standards should be recorded on the digestion log with the samples.

13.3 Any run comments should be written on the raw data for the analysis and on the run log in the LIMS.

13.4 Annual bottle calibration verifications must be documented in the Mercury Bottle

calibration log.

14.0 DATA REVIEW AND REPORTING

14.1 All samples should be updated to QC batches in the LIMS system. The analyst is responsible for reviewing all data for compliance with the QC outlined in this SOP. They are responsible for making sure that the raw data is fully documented and it is loaded into the LIMS system. They are responsible for submitting samples for redigestion and reanalysis, when appropriate.

14.2 After the analyst review is completed, the supervisor or a designated reviewer shall review the run for technical compliance to the SOP. The reviewer is also responsible for making sure that the QC calculations are done correctly and that appropriate flags are added.

14.3 After the reviewer completes their review, the data is released for client access in the LIMS. The raw data and the run log are submitted to the area manager. The manager periodically does an additional review on data for technical completeness. Any hardcopy raw data is transferred to the report generation department for scanning and storage. Instrument data is transferred electronically.

15.0 POLLUTION PREVENTION & WASTE MANAGEMENT

15.1 Users of this method must perform all procedural steps in a manner that controls the creation and/or escape of wastes or hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids or solids to the environment must be followed. All method users must be familiar with the waste management practices described in section 16.2.

15.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the waste management SOP, EHS 004. This document describes the proper disposal of all waste materials generated during the testing of samples as follows:

15.2.1 Non hazardous aqueous wastes.

15.2.2 Hazardous aqueous wastes.

15.2.3 Chlorinated organic solvents.

15.2.4 Non-chlorinated organic solvents.

15.2.5 Hazardous solid wastes.

15.2.6 Non hazardous aqueous wastes.

16.0 ADDITIONAL REFERENCES

16.1 Leeman Hydra II instrument manual.

File: EMA226-07
Pub. Date: 06/24/10
Rev. Date: 04/12/13

Lab Manager Nancy Cole

QA Manager

Effective Date: 5-6-13

TEST NAME: METALS BY INDUCTIVELY COUPLED PLASMA – MASS SPECTROMETRY (ICP-MS)

METHOD REFERENCE: SW846 6020A, Revision 1, February 2007.

Revised Sections: ***Section 11.12. Table 2B***
Added Section: ***none***

1.0 SCOPE AND APPLICATION

1.1 This method is applicable for the determination of total and dissolved metals in water samples and in waste extracts or in solid or aqueous digests.

2.0 SUMMARY

2.1 Samples are prepared for analysis by digestion. The prepared samples are introduced into a radiofrequency plasma by pneumatic nebulization. There the energy transfer processes cause desolvation, atomization, and ionization. The ions are extracted from the plasma through a differentially pumped vacuum interface and separated on the basis of their mass to charge ratio by a quadrupole mass spectrometer. The ions transmitted through the quadrupole are detected by an electron multiplier and the ion information is processed by a data handling system.

3.0 REPORTING LIMIT AND METHOD DETECTION LIMIT

3.1 Reporting Limit. Current reporting limits for this method have been established at the levels listed in Table 1. The reporting limits are dependent upon the metal being analyzed and are in all cases greater than the IDL and the MDL for each element. Note: Many clients require special reporting limits. Refer to the scheduling sheets and check with the metals supervisor for additional information.

3.2 Method Detection Limit. Experimentally determine MDLs using the procedure specified in 40 CFR, Part 136, Appendix B. This value represents the lowest reportable concentration of an individual compound that meets the method qualitative identification criteria.

3.2.1 Experimental MDLs must be determined annually for this method.

4.0 DEFINITIONS

BATCH. A group of 20 samples or less that behave similarly with respect to the sampling or the testing procedures being employed and which are processed as a unit within a 24 hour period. For QC purposes, if the number of samples in a group is greater than 20, then each group of 20 samples or less will all be handled as a separate batch.

CALIBRATION CHECK STANDARD. The calibration check standard is a mid-range calibration standard. It is recommended that the calibration check standard be run at a frequency of 10 percent or every 2 hours during an analysis run, whichever is more frequent, and at the end of the analysis sequence. For this method, the mid-level calibration check standard criteria is ± 10 percent of the true value and the relative standard deviation for the replicates that are greater than 5 times the reporting limit is less than 5 percent. The exception to this rule is if the recovery on the calibration check standard is high and the samples to be reported are less than the reporting limit.

EXTERNAL CHECK STANDARD. The external check standard is a standard from a separate source than the calibration curve that is used to verify the accuracy of the calibration standards. It must be run after each calibration. The external check standard criteria is ± 10% of the true value and the replicates that are greater than 5 times the reporting limit should have a relative standard deviation of less than 5 percent. If the external check is outside of the control limits for a given parameter, all samples must be reanalyzed for that parameter after the problem has been resolved.

SPIKE BLANK OR LAB CONTROL SAMPLE. Digest and analyze a laboratory control sample or spike blank with each set of samples. A minimum of one lab control sample or spike blank is required for every 20 sample batch. A sample batch is defined as a maximum of 20 field samples in a preparation batch over a time period of 24 hours. Assess laboratory performance against the control limits of 80 to 120 percent. In house limits should also be generated once sufficient data is available to support the default limits. If the lab control or spike blank is outside of the control limits for a parameter, all samples must be redigested and reanalyzed for that parameter. The exception is if the lab control or spike blank recovery is high and the results of the samples to be reported are less than the reporting limit. In that case, the sample results can be reported with no flag.

MATRIX: The component or substrate (e.g., water, soil) which contains the analyte of interest.

MATRIX DUPLICATE: A duplicate sample is digested at a minimum of 1 in 20 samples. The relative percent difference (RPD) between the duplicate and the sample should be assessed. The duplicate RPD is calculated as shown below. Assess laboratory performance against method limits. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of ± the reporting limit, then the duplicate is considered to be in control.

$$\frac{(|\text{Sample Result} - \text{Duplicate Result}|) \times 100}{(\text{Sample Result} + \text{Duplicate Result})/2} = \text{Duplicate RPD}$$

MATRIX SPIKE: The laboratory must add a known amount of each analyte to a minimum of 1 in 20 samples. The matrix spike recovery is calculated as shown below. Assess laboratory performance against default limits of 75 to 125 % recovery. In house limits should be generated once sufficient data is available. If a matrix spike is out of control, then the results should be flagged with the appropriate footnote. If the matrix spike amount is less than one fourth of the sample amount, then the sample cannot be assessed against the control limits and should be footnoted to that effect.

$$\frac{(\text{Spiked Sample Result} - \text{Sample Result})}{(\text{Amount Spiked})} \times 100 = \text{Matrix Spike Recovery}$$

MATRIX SPIKE DUPLICATES: Intralaboratory split samples spiked with identical concentrations of target analyte(s). The spiking occurs prior to sample preparation and analysis. They are used to document the precision and bias of a method in a given sample matrix.

METHOD BLANK. The laboratory must digest and analyze a method blank with each set of samples. A minimum of one method blank is required for every 20 sample batch. If no digestion step is required, then the method blank is equivalent to the reagent blank. The method blank must contain the parameter of interest at levels of less that the reporting limit for that parameter. If the method blank contains levels over the reporting limits, the samples must be redigested and reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the method blank level. In addition, if all the samples are less than a client required limit and the method blank is also less than that limit, then the results can be reported as less than that limit.

METHOD DETECTION LIMITS (MDLS). The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte. MDLs should be determined approximately once per year for frequently analyzed parameters.

REAGENT BLANK. The reagent blank is a blank that has the same matrix as the samples, i.e., all added reagents, but did not go through sample preparation procedures. The reagent blank is an indicator for contamination introduced during the analytical procedure. (Note: for methods requiring no preparation step, the reagent blank is equivalent to the method blank.) Either a reagent blank or a method blank must be analyzed with each batch of 20 samples or less. The concentration of the analyte of interest in the reagent blank must be less than the reporting limit for that analyte. If the reagent blank contains levels over the reporting limits, the samples must be reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the reagent blank level. In addition, if all the samples are less than a client required limit and the reagent blank is also less than that limit, then the results can be reported as less than that limit.

REAGENT GRADE. Analytical reagent (AR) grade, ACS reagent grade, and reagent grade are synonymous terms for reagents which conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.

REAGENT WATER. Water that has been generated by any method which would achieve the performance specifications for ASTM Type II water.

STANDARD ADDITION. The practice of adding a known amount of an analyte to a sample immediately prior to analysis. It is typically used to evaluate interferences.

STANDARD CURVE: A plot of concentrations of known analyte standards versus the instrument response to the analyte. Calibration standards are prepared by successively diluting a standard solution to produce working standards which cover the working range of the instrument. Standards should be prepared at the frequency specified in the appropriate section. The calibration standards should be prepared using the same type of acid or solvent and at the same concentration as will result in the samples following sample preparation. This is applicable to organic and inorganic chemical analyses.

5.0 HEALTH & SAFETY

5.1 The analyst must follow normal safety procedures as outlined in the Accutest Health and Safety Plan and Personal Protection Policy, which include the use of safety glasses and lab coats. In addition, all acids are corrosive and must be handled with care. Flush spills with plenty of water. If acids contact any part of the body, flush with water and contact the supervisor.

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical must be treated as a potential health hazard. Exposure to these reagents must be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets must be made available to all personnel involved in these analyses.

6.0 PRESERVATION & HOLDING TIME

6.1 All water samples should be preserved with nitric acid to a pH of 2 or less. All solid samples should be stored in a refrigerator at 4 degrees C until digestion.

6.2 All samples should be analyzed within 6 months of the date of collection.

7.0 INTERFERENCES

7.1 Several types of interferences can cause inaccuracies in trace metals determinations by ICP-MS. These interferences are discussed below.

7.2 Isobaric elemental interferences are caused by isotopes of different elements which form singly or doubly charged ions of the same nominal mass-to-charge ratio and which cannot be resolved by the mass spectrometer in use. If isobaric interferences are present in the ion being analyzed, then the data must be corrected by measuring the signal from another

isotope of the interfering element and subtracting the appropriate signal ratio from the element of interest.

7.3 Abundance sensitivity is a property that defines the degree to which the wings of a mass peak contribute to adjacent masses and is affected by ion energy and quadrupole operating pressure. Wing overlap interferences may result when a small ion peak is being measured next to a large one. Spectrometer resolution should be adjusted to minimize these interferences.

7.4 Isobaric polyatomic ion interferences are caused by ions consisting of more than one atom which have the same nominal mass-to-charge ratio as the isotope of interest, and which cannot be resolved by the mass spectrometer in use. Refer to method 200.8 and 6020 for lists of common interferences and correction equations to be applied. If these interferences cannot be avoided by the use of different isotopes, then correction equations should be applied to the data. Alternatively, collision/reaction cell technology can be applied to physically and chemically remove interferences.

7.5 Physical interferences can occur during the transfer of the solution to the nebulizer (viscosity effects).

7.6 Memory interferences can be caused by build up on the sampler and skimmer cones, and from buildup of sample material in the torch and spray chamber. Some elements, such as mercury, can suffer from severe memory effects. In that case, gold is added to the rise solution to decrease the Hg rinse out time.

8.0 APPARATUS

8.1 Currently there are two ICP-MS instruments available for use in the lab. The first is a Thermo Elemental X2 (upgraded from an X5) with XI interface. This instrument has been designed to handle environmental matrices and is interfaced with an ESI fast autosampler. The second is an Aglilent 7700x ICP-MS with collision/reaction cell capacity and and HMI (High matrix interface) and the associated autosampler.

8.2 Class A volumetric glassware as needed and instrument autosampler tubes.

8.2.1 All glassware must be washed with soap and tap water and then soaked in a 10% nitric acid bath for several hours. It must then be rinsed at least 3 times with distilled, deionized water.

8.3 Polypropylene bottles for standard storage. These bottles must also be cleaned as outlined above.

9.0 REAGENTS

9.1 All chemicals listed below are reagent grade unless otherwise specified. Deionized water must be used whenever water is required. Note: All reagents can be scaled up or down proportionately if different final volumes are required.

9.2 Hydrochloric acid, trace metals grade.

9.3 Nitric acid, trace metals grade. Note – ultra trace grade may be required if lower detection limits than normal are needed.

9.4 Standard stock solutions available from Inorganic Ventures, Ultra Scientific, MV Laboratories or equivalent. Note: All standards must be ICP-MS quality standards or must be demonstrated to be free of interferences at the levels of use. Standards should come labeled with an expiration date and certificate of concentrations from the manufacturer. If both of these items are not received, then the manufacturer should be contacted before use of the standard.

9.5 Calibration Standards: These can be made up by diluting the stock solutions to the appropriate concentrations. Fresh calibration standards should be prepared a minimum of every two weeks. They must be monitored weekly for stability.

9.5.1 Standards should be made in a low acid matrix. Concentrations of 1 to 2 percent nitric acid and 0 to 0.6 percent hydrochloric acid are suggested, although any acid concentration that provides good analytical results may be used. High chloride concentrations may cause interferences so chloride concentrations should be limited. HCl may be omitted if silver and antimony are not elements of interest.

9.5.2 Refer to the standards book for the make-up and concentrations of standards and stock solutions being used to calibrate the ICP-MS. Suggested standard levels are shown in Table 2.

9.5.3 All standards should be stored in acid washed FEP fluorocarbon bottles.

9.6 Mass Calibration Standard, Thermo ICP-MS. This standard must contain a spread of elements across the full mass range, and must include Li and U. All elements must be at a concentration to be measured in pulse counting mode. A 20 ppb solution is recommended. An acid matrix of 1% nitric and 0 to 0.6% HCl is recommended.

9.7 Detector Plateau Standard, Thermo ICP-MS. This standard is used to optimize the voltage range for analysis and it is recommended that 3 different masses in the low and mid mass range be included, with concentrations to be measured in the pulse counting mode. A solution containing Be (9), Co (59), and In (115) at approximately 20 ppb should generally work for this application. An acid matrix of 1% nitric and 0 to 0.6% HCl is recommended.

9.8 Thermo Cross Calibration Standard. This standard is used to make sure that the counts between the pulse and analog modes are properly aligned. It must contain elements over the range of the masses and must include Li and U. All elements must be at a concentration to be measured both in pulse and analog mode. Lower concentrations are recommended for

the high masses and higher concentrations are recommended for the low masses. One suggested solution for cross calibration contains 500 ppb of most elements plus 100 ppb of U, Ce, and Li.

9.9 Aglient P/A Factor and Tuning/Performance Check Solution. Mix 1.0 ml of PA Tuning 1 solution and 1.0 ml of PA Tuning 2 solution (available from Aglient, part number 5188-6524) and bring to 100 ml final volume with a solution of 1% nitric acid and 0.6% HCl. This final solution contains 200 ppb of As, Be, Cd, Zn; 100 ppb of Mg, Ni, and Pb; 50 ppb of Al, Ba, Bi, Co, Cr, Cu, In, Li^6, Lu, Mn, Na, Sc, Sr, Th, Tl, U, and V; and 25 ppb of Y and Yb; 100 ppb of Ge, Mo, Pd, Ru, Sb, Sn ; and 50 ppb of Ir and Ti.

9.10 Tuning Standard, Thermo ICP-MS. This solution is used to verify mass calibration and thermal stability and must contain a mix of elements representing all of the mass regions of interest. Recommended elements include 200.8 tuning elements (Be, Mg, Co, In, and Pb) at 10 ppb in a 1% nitric solution plus 10 ppb of Li, Tl, U, and Ce.

9.11 Tuning Standard, Agilent ICP-MS. This solution is used to verify mass calibration and thermal stability and must contain a mix of elements representing all of the mass regions of interest. Elements include 1 ppb Ce, Co, Li, Mg, Tl, and Y.

9.12 Internal Standards. Internal standards are added to all calibration standards, quality control, and samples during analysis, normally using a second channel of the peristalic pump and a mixing manifold. At a minimum, the internal standard solution must contain Sc, Y, In, Tb, and Bi.

9.12.1 For the Thermo instrument, a solution containing 20 ppb of 6Li, Sc, Y, Rh, In, Tb, Ho, and Bi in 1% nitric acid is recommended. Refer to Table 3.

9.12.2 For the Aglient instrument, a solution containing 1 ppm of Li, Sc, Rh, In, Tb, Ho, and Bi and 2 ppm of Ge in 1 % nitric is recommended. Refer to Table 3.

9.13 Calibration /Rinse Blank. The calibration and rinse blanks are prepared by diluting acids to the same concentrations found in the standards. The calibration blank is used to establish the analytical calibration curve and the rinse blank is used to flush the instrument between samples in order to reduce memory interferences.

9.14 Continuing Calibration Verification Check (CCV). This solution is prepared by adding either mixed or single element metals solutions to a solution containing the same acid matrix as the calibration standards. The metals should be at concentrations near the middle of the calibration curve. (Note: This check is run after the calibration, after every 10 samples or every 2 hours during an analysis run, whichever is more frequent, and at the end of the sample run.) Refer to Table 2 for suggested concentrations for the CCV.

9.14.1 Method 6020 does not specify the source of the CCV check. However, it is recommended that these be prepared from the same source as the calibration as it required in method 200.8

9.15 Matrix Spike and Spike Blank Solution. Suggested levels for the final concentrations of the spike are shown in Table 4. This solution is prepared by adding either mixed or single element metals solutions to a solution containing 1 percent nitric acid and 0 to 0.6 % HCl and

diluting to a fixed final volume with this acid mixture. 0.5 ml of this stock solution should be added to spike blank and the matrix spike before they are digested and brought to a final volume of 50 ml.

9.16 Lab Control Solution. This solution is prepared by adding either mixed or single element metal solutions to a solution containing 2 percent nitric acid and 0 to 0.6 % HCl and diluting to a fixed final volume with this acid mixture. 50 ml of this solution is digested and brought to a final volume of 50 ml. The lab control and spike blank can be used interchangeably for aqueous matrices for this method.

9.17 Interference Element Check Solutions. The purpose of the ICSA and ICSAB solutions is to demonstrate the magnitude of interferences and provide an adequate test of any corrections. It is recommended that the following solutions be purchased commercially.

9.17.1 ICSA Solution. The ICSA solution contains only the interfering elements. The recommended concentrations are shown below. The ICSA solution must be made fresh weekly.

Al	100 mg/L
Ca	100 mg/L
Fe	100 mg/L
Mg	100 mg/L
Na	100 mg/L
P	100 mg/L
K	100 mg/L
S	100 mg/L
C	200 mg/L
Cl	1000 mg/L
Mo	2.00 mg/L
Ti	2.00mg/L

9.17.2 ICSAB Solution. The ICSAB solution contains both the interferents and the analytes of interest. The recommended concentrations are shown below. The ICSAB solution must be made fresh weekly.

Al	100 mg/L
Ca	100 mg/L
Fe	100 mg/L
Mg	100 mg/L
Na	100 mg/L
P	100 mg/L
K	100 mg/L
S	100 mg/L
C	200 mg/L
Cl	1000 mg/L
Mo	2.00 mg/L
Ti	2.00mg/L
As	0.020 mg/l
Cd	0.020 mg/l
Cr	0.020 mg/l
Co	0.020 mg/l
Cu	0.020 mg/l
Mn	0.020 mg/l
Ni	0.020 mg/l
Ag	0.020 mg/l
Zn	0.020 mg/l

9.18 Initial Calibration Verification (ICV) or Quality Control Sample (QCS). The metals in this solution should be at final concentrations that are at the mid-point of the calibration curve. This solution is prepared by adding either mixed or single element metals solutions to a solution containing 1 percent nitric acid and 0 to 0.6 percent hydrochloric acid and diluting to a fixed final volume with this acid mixture. Note: The ICV sample must be from a separate source from the calibration standards. This solution should be stored in a FEP fluorocarbon or previously unused polyethylene bottle.

9.19 CRI Standards (also referred to as LLCCV). The CRI standard must contain the elements of interest at (or below) the reporting limit for each element. The CRI level is at the reporting limit as shown in Table 1. This should be prepared by diluting calibration standard(s) to the reporting limit level for each element. They should be made in the same matrix as the calibration standards. Note: The CRI must be verified at the RL before any dilutions are applied. For example, Be is verified at 0.5 ug/l and the water reporting limit is 1.0 ug/l with a 1:2 dilution.

9.20 Liquid Argon or Argon Gas. Argon is provided by Air Products in the large outdoor tank. No lab monitoring of the tank is normally necessary.

9.21 Helium Gas. Required for running the reaction cell on the Agilent 7700X.

10.0 INITIAL INSTRUMENT SET-UP PROCEDURE FOR THE THERMO ICP-MS.

10.1 A general procedure on how to operate the Thermo X2/5 ICP-MS is given below. Refer to the X5 operation manual for further details.

10.2 Before bringing up the instrument, make sure that the lines, the torch, the nebulizer, and the spray chamber are clean, and that there are no leaks in the torch area. Make sure that the Faraday cage is in the forward position and that the cage door is closed.

10.3 Turn on the recirculating cooler. Verify that the liquid argon is turned on.

10.4 Engage the peristaltic pump.

10.5 Put a new solution of acid rinse into the rinse reservoir. (Note: the composition of the rinse solution may be periodically changed to minimize sample introduction problems and sample carryover.) Make sure that sufficient internal standard solution is present.

10.6 Turn on the instrument by clicking on the ON button. The instrument will automatically go through the start-up cycle which lasts approximately 90 to 120 seconds and let the instrument warm up for at least 30 minutes. Go to the instrument icon and the configuration page and make sure that the proper configurations and accessories are selected.

10.7 Every one to two days or as needed, tune the instrument. Tuning must always be done after moving the position of the torch or the cones. Tuning can be done either manually or by following autotune procedures. It is recommended that autotune procedures be followed initially and then manual tuning be done as a second step. The purpose of tuning is to optimize the instrument for the highest sensitivity while obtaining low levels of oxides and doubly charged species. In general, the high masses have good sensitivity while the lower masses have less sensitivity, so it is recommended that the instrument be tuned with more emphasis on the sensitivity of low to mid-range masses. After the tune is complete, make sure to save the optimized parameters.

10.7.1 The major parameters are the parameters that have the greatest effect on signal stability and sensitivity. If tuning manually, start with D1, then extraction, Lens1, focus, and pole bias. Monitor how the signal changes with each adjustment and adjust for the maximum signal and minimum oxide ratio.

10.7.2 The minor parameters are the parameters that are used to make smaller changes in the tune. Normally the horizontal and vertical positions are the minor parameters that need adjustment.

10.7.3 Click RTD (real time display) to monitor the signal as the tuning is done.

10.7.4 Monitor the tuning solution to make sure that masses are being properly assigned. If the mass calibration has shifted by more than 0.1 amu from unit mass, then update the mass calibration as described in 10.8.

10.8 Approximately once every 6 months or as needed, update the mass calibration. (The mass calibration must be adjusted if it has shifted by more than 0.1 amu from the unit mass.) Set up an experiment with the sample label of mass calibration and the type instrument set-up. Then go to the advance properties and click the update mass calibration option. Aspirate the

mass calibration solution (see section 9.6) and queue the experiment. After the calibration is complete, then go to the instrument icon and click on the mass calibration that has just been performed. Look for peak widths of approximately 0.75 amu at 5% peak height with an error of < 0.2 amu for optimal performance. If it is not within this range, check with the area supervisor before proceeding.

10.9 Approximately once per month, or more often if the detector is getting old, perform a detector plateau calibration. Set up an experiment with the sample label of detector plateau and the type instrument set-up. Go to the advance properties and check the Plateau detector box. Set the masses for the elements in the Detector plateau solution (see section 9.7) and enter start and end voltages approximately 400 volts below and above the current pulse counting HT voltage. The voltage step should be set at 20. Aspirate the detector plateau solution and queue the experiment. After the experiment is complete, go to the instrument icon and click on the detector plateau that has just been performed. Determine the value at approximately 90 percent on the plateau and enter the PC voltage on the tune page under global.

10.10 On a daily basis, perform an instrument cross calibration. The purpose of the cross calibration is to set the appropriate factor for aligning the pulse and analog counts. Set up an experiment with the sample label of cross calibration and the type instrument set-up. Go to the advanced properties and check the detector calibrate box and set the offset mass to 220. It is recommended to also set up a second sample with a survey run after the initial cross calibration. Aspirate the cross calibration check solution (see section 9.8) and queue the experiment. When the experiment is complete, go to the instrument icon and click on the detector cross calibration that was just performed. Check that the factors are < 40000. Go to the experiment and make sure that the analog and pulse counts are lining up well over the mass range.

10.11 Before calibrating, run and print out a performance test. This must include the following items.

10.11.1 Demonstrate instrument stability by running the tuning solution a minimum of five times. Relative standard deviations of the absolute signals must be less than 5 percent for all elements in the tuning solution. If this criteria is not met, correct the problem and then repeat the stability test. Print the results of this test and store with the raw data for the run.

10.11.2 Verify acceptable mass calibration by running the tuning solution and monitoring the peak width measured at 5% of peak maximum for 7Li, 24Mg, 25Mg, 26Mg, 115In, 206Pb, 207Pb, 208Pb, and 238U. If the peak widths are outside of the range of 0.65 to 0.85 and the masses are off more than 0.1 amu, then redo the mass calibration as outlined in 10.8 before proceeding.

10.12 Calibrate the instrument using a minimum of a calibration blank and three non-zero standards that bracket the desired sample concentration range. (Note: The calibration standards may be included in the autosampler program or they may be run separately.) A correlation coefficient of 0.998 or better must be obtained using a first order (linear) curve fit. A minimum of three replicate integrations are required for all data acquisitions.

10.12.1 In between each analysis of a separate standard or sample, a rinse blank must be run through the lines of the sample introduction system. Each sample or standard should be aspirated for a minimum of 30 seconds prior to the acquisition of data to allow equilibrium to be established.

10.12.2 Alternatively, a calibration may be done with a blank and a high standard. This calibration must then be confirmed with low level and mid-level calibration standards that are run immediately after the calibration is complete. The low level check must have recoveries within 70 to 130 to be acceptable and the mid-level check must have recoveries within 90 to 110 to be acceptable.

10.13 After the instrument is properly calibrated, begin by analyzing the ICV solution. The ICV must be run after each calibration. For the ICV, all elements to be reported must be within 10 percent of the true value and the replicates that are greater than 5 times the reporting limit should have a relative standard deviation of less than 5 percent. If the ICV is outside of criteria, then the problem must be identified and corrected before samples can be run and reported for the element(s) that are outside of criteria. Correction of the problem can be verified by rerunning the check standard(s) and showing that they meet QC criteria.

10.13.1 An ICB may be run after the ICV, but is not required for this method. If it is run, then all elements must be less than reporting limit (lower limit of quantitation) for each element.

10.13.2 Run the CRI (LLCCV) solution right after the ICV and ICB, (or any other place at the beginning of the run after the ICV, ICB and before any real samples are analyzed). For the CRI, all elements of interest must be within 30% of the true value or within client specified limits.

10.14 Then analyze the CCV and CCB check standards. For the CCV, all elements to be reported must be within 10 percent of the true value and the replicates that are greater than 5 times the reporting limit should have a relative standard deviation of less than 5 percent. For the CCB, all elements to be reported must normally be less than the reporting limit (lower limit of quantitation). If either the CCV or CCB do not meet criteria, than elements failing this criteria must not reported in the area bracketed by this QC.

10.14.1 The internal standard levels in the CCV and CCB must also be within 30% of the internal standard level for the initial calibration. If they are outside of these levels, then no samples can be reported in the area bracketed by this QC.

10.15 After the initial QC is completed and before any samples are analyzed, the ICSA and ICSAB solutions must be analyzed. The method does not list specific criteria for the ICSA and ICSAB, but in house criteria will be applied. For all the spiked elements, the analyzed results must be within 20 percent of the true results. For unspiked elements, the interfering element solution should contain less than the absolute value of 3 times the reporting limit for each element. If these criteria are not met, then samples with significant interferences can not be reported until the correction factors are optimized and the ICSA and ICSAB are within specifications.

10.15.1 If the run is longer than 12 hours, a second ICSA, ICSAB pair must be analyzed before the next 12 hours is started.

10.15.2 If mass changes are made for the analysis of an element, all QC criteria must be met for the new mass and it must be verified that appropriate correction factors are in place.

10.16 After the initial analytical quality control has been analyzed, the samples and the preparation batch quality control should be analyzed. Depending on the type of digestion and the sample matrix, samples and the associated QC should normally be diluted by a factor of from 2 to 5 before analysis. This dilution factor should be indicated in the sample ID file on the instrument.

10.16.1 Each sample analysis must be a minimum of 3 integrations. For samples containing levels of elements greater than approximately 5 times the reporting limits, the relative standard deviations for the replicates should be less than 10%. If not, reanalyze the sample. If, upon reanalysis, the RSDs are acceptable, then report the data from the reanalysis. If RSD's are not acceptable on reanalysis, then the results for that element may, on the reviewer's discretion, be footnoted that there are possible analytical problems indicated by a high RSD between replicates. In some cases, an additional dilution analysis may be needed. Check with the area supervisor or manager for additional information.

10.16.2 The internal standard levels must be monitored for all samples and quality control. If the internal standard is not within 30% of the internal standard level for the initial calibration blank, then the sample must be diluted by a factor of 5 to bring the internal standard to within the correct range. If the internal standard is still outside of the range after the initial 1:5 dilution, then additional dilutions must be done until the internal standard is within the appropriate range.

10.16.2.1 If an internal standard is present in a sample, then do not use that internal standard. For example, Y is sometimes seen in real samples. If the Y recoveries are high relative to the other internal standards, then do not use the Y internal standard.

10.16.3 For any readings that exceed the linear range for a given element, a dilution is required. After a high reading, the sample following the high one must be examined for possible carryover. A verification may be necessary by rinsing the lines with an acid solution and then rereading the sample.

10.16.4 Indicate dilution factors for samples using df followed by the dilution factor after the sample ID. There should be a space between the sample number and the df.

10.17 Between each sample, flush the nebulizer and solution uptake system with a blank rinse solution for a minimum of 30 seconds or for the required period of time to ensure that analyte memory effects are not occurring. (60 seconds is recommended for normal methods excluding Hg and B. Longer times may be needed when Hg and B are being analyzed.)

10.18 Analyze the continuing calibration verification solution and the continuing calibration blank after every ten samples and at the end of the sample run.

10.18.1 For the CCV, all elements to be reported must be within 10 percent of the true value and the replicates that are greater than 5 times the reporting limit should have a relative standard deviation of less than 5 percent. If the CCV solution is not within 10 percent of the true value, no samples can be reported in the area bracketed by the failing CCV for the failing element.

10.18.2 For the CCB, all elements to be reported must be less than the reporting limit (lower limit of quantitation).

10.18.3 The internal standard levels in the CCV and CCB must also be within 30% of the internal standard level for the initial calibration. If they are outside of these levels, then no samples can be reported in the area bracketed by this QC.

10.19 The CRI (LLCV) must be analyzed at the end of each calibration (analysis) batch. The acceptance criterion for the CRI check is 70 to 130% recovery. If an element does not meet this criterion, then all samples for that element in the concentration range between the CRI and the CCV must be reanalyzed. Samples containing concentrations higher than the CCV may be reported as long as CCV criteria are met.

10.19.1 More frequent CRI (LCCV) checks may be analyzed during the course of the run if system stability at the low end of the calibration is questionable or if the lab wants to ensure that fewer samples will have to be submitted for reanalysis if there is a failed CRI at the end of a run.

10.19.2 It is recommended that the CRI check be run bracketing every 4 to 8 hour period of analysis. It may be run as frequently as every 10 samples if the supervisory staff deems that this is necessary.

10.20 After the run is completed, convert the data file to a CSV format using the option on the results screen. First save the file on the local drive using the file naming system described below. Update the run in the LIMS and enter the run name into the workgroup using lower case characters. Then copy the data from the local drive to the LIMS drive.

10.20.1 The file should be named as followed- initial instrument indicator (X), date (MMDD), year, run type (soil, water, or mixed), and sequential run number for that day. For example, the first water run from 12/17/02 would be designated X121702w1.csv.

10.21 Calculations are done in the LIMS using the calculations shown below.

10.21.1 Calculation for aqueous samples.

original sample concentration of metal (µg/l) =

$$\frac{\text{(conc. in the digestate (µg/l)) x (final digestate volume (ml))}}{\text{(Initial sample volume (ml))}}$$

10.21.2 Calculation for solid samples.

original sample concentration of metal (mg/kg) =

$$\frac{\text{(conc. in the digestate (µg/l)) x (final digestate volume (ml))}}{\text{(Initial sample weight (g)) x (\%sol/100)}}$$

10.22 At the end of the analysis day the ICP-MS must be brought down using the following sequence.

- Rinse the tip in a solution of 4 percent nitric acid and 2 percent hydrochloric acid for 10 minutes and in DI water for 20 minutes. (Note: a stronger acid solution may be needed depending on the matrix of the samples that were analyzed.)
- Turn off the plasma using off button.
- Release the tension on the pump tubing.
- Turn off the cool flow and the printer.
- Turn off the monitor.

11.0 INITIAL INSTRUMENT SET-UP PROCEDURE FOR THE AGILENT 7700X ICP-MS

11.1 A general procedure on how to operate the Agilent 7700X ICP-MS is given below. Refer to the operation manual for further details.

11.2 Before bringing up the instrument, make sure that the lines, the torch, the nebulizer, and the spray chamber are clean, and that there are no leaks in the torch area.

11.3 Turn the vacuum pump and the heat exchanger on and verify that the liquid argon is turned on and the helium gas is turned on.

11.4 Connect the pump tubing and engage the peristaltic pump.

11.5 Put a new solution of acid rinse into the rinse reservoir. (Note: the composition of the rinse solution may be periodically changed to minimize sample introduction problems and sample carryover.) Make sure that sufficient internal standard solution is present.

11.6 Open the ICP-MS Mass Hunter Top software. Click on the instrument and open the instrument control panel. Click the plasma on. The instrument will automatically go through the start-up cycle. Then let the instrument warm up for at least 30 minutes.

11.7 Every one to two days or as needed, tune the instrument. Tuning must always be done after moving the position of the torch or the cones. Tuning can be done either manually or by following autotune procedures. It is recommended that autotune procedures be followed initially and then manual tuning be done as a second step. The purpose of tuning is to

optimize the instrument for the highest sensitivity while obtaining low levels of oxides and doubly charged species. After the tune is complete, make sure to save the optimized parameters.

11.7.1 Open the ICP-MS top software, client on the instrument, and open the ICP-MS tuning page.

11.7.2 Click file and open the NOGAS.U file. Keep the internal standard line in a solution of 1% nitric acid and 0.6% hydrochloric acid. Using the ALS (autosampler) send the probe to the 1 ppb Aglient tuning solution (see 9.10) . On the tuning page, click start under the RTD window to see the counts and RSD values. Do not start the tune process until the count and mean have similar readings and the RSD is < 5%. The counts per second values should be > 40000 for all masses. Click stop under RTD window.

11.7.3 On the tuning page, click Autotune, type the date on the pop-up window, and click OK. This will perform the tuning of the instrument using both the NOGAS and the Helium mode. Print the tune and save it as MAXXXXX_Tune.pdf.

11.8 On a daily basis, perform a cross calibration to align the pulse and analog signals.

11.8.1 Go to the ICP-MS Top portion of the software and load the method P-A-M. Be sure that the NOGAS.U file is open.

11.8.2 Using ALS, send the probe to the P/A factor solution. This solution is diluted from a concentrated mixture of PA Tuning 1 and PA Tuning 2 solution which can be purchased from Agilent Technologies.

11.8.3 In the ICP-MS Tuning page, under the Tune, click P/A factor. Click run in the popup window. Some elements may have too low or too high sensitivity. In this case, rerun the P/A factor process one or more times by clicking "Merge in the current data" in the same pop-up window.

11.8.4 Print and save the P/A factor report as MAXXXX_PA.pdf.

11.9 Before calibrating, run and print out a performance test. This must include the following items.

11.9.1 Demonstrate instrument stability by running the tuning solution a minimum of five times. Relative standard deviations of the absolute signals must be less than 5 percent for all elements in the tuning solution. If this criteria is not met, correct the problem and then repeat the stability test. Print the results of this test and store with the raw data for the run.

11.9.2 Verify acceptable mass calibration by running the tuning solution and monitoring the peak width measured at 5% of peak maximum for 7Li, 24Mg, 25Mg, 26Mg, 115In, 206Pb, 207Pb, 208Pb, and 238U. If the peak widths are outside of the range of 0.65 to 0.85 and the masses are off more than 0.1 amu, then redo the mass calibration as outlined in 10.8 before proceeding.

11.9.3 To run this performance test, load the PERF.m method. Be sure that the NOGAS.U file is open. Using the ALS, send the probe to the 20 ppb tune solution. On the ICP-MS tuning page, click QC and then click "QC Tune report" from the drop-down menu. This will start the performance report. At the print-out window, click on "wait, collect" to combine the multiple pages of the pdf together.

11.9.4 To run the 5 replicate stability check, keep the Perf.m Method open. This method is set up to run 5 replicates. Set up and run the sequence. On the data analysis page, select CPS and CPS % RSD for all replicates. After the samples are finished, click on Export Data Analysis table with transposition.

11.9.5 Click print and combine the portions of the performance test together in a PDF convertor window and then save this as MAXXXX_perf.pdf.

11.10 Before starting sample analysis, set up the internal standards. Internal standards are added to all calibration standards, quality control, and samples during analysis, normally using a second channel of the peristaltic pump and a mixing manifold. Refer to Table 3 and Section 9.12 for additional information.

11.11 To start running samples, open the ICP-MS Top window, and then click method followed by load. Selection the method from the list. The normal method used for 6020 analyses is ACNJ6020.m

11.11.1 Click sequence and then click load. Select the template from the list. For 6020 anayses, the normal template is ACNJ6020.s

11.11.2 Click Edit the sample log table and type in the standards and samples. Save the sequence as MMDDYY.s. Be sure to load the saved sequence again. Click Run to start.

11.11.2.1 At the pop-up window, enter the data bach directory line type file name as C:\ICPMH\1\DATA\MAXXXXX.B\. Click on run sequence. This will open the data analysis page. (This page can be modified using the DA Method Editor).

11.12 Calibrate the instrument using a minimum of a calibration blank and three non-zero standards that bracket the desired sample concentration range. The lowest non-zero standard must be at or lower than the RL or LOQ levels for all the elements. (Note: The calibration standards may be included in the autosampler program or they may be run separately.) A correlation coefficient of 0.998 or better must be obtained using a first order (linear) curve fit. A minimum of three replicate integrations are required for all data acquisitions.

11.12.1 In between each analysis of a separate standard or sample, a rinse blank must be run through the lines of the sample introduction system. Each sample or standard should be aspirated for a minimum of 30 seconds prior to the acquisition of data to allow equilibrium to be established.

11.12.2 Alternatively, a calibration may be done with a blank and a high standard. This calibration must then be confirmed with low level and mid-level calibration standards that are run immediately after the calibration is complete. The low level check must have recoveries within 70 to 130 to be acceptable and the mid-level check must have recoveries within 90 to 110 to be acceptable.

11.13 After the instrument is properly calibrated, begin by analyzing the ICV solution. The ICV must be run after each calibration. For the ICV, all elements to be reported must be within 10 percent of the true value and the replicates that are greater than 5 times the reporting limit should have a relative standard deviation of less than 5 percent. If the ICV is outside of criteria, then the problem must be identified and corrected before samples can be run and reported for the element(s) that are outside of criteria. Correction of the problem can be verified by rerunning the check standard(s) and showing that they meet QC criteria.

11.13.1 An ICB may be run after the ICV, but is not required for this method. If it is run, then all elements must be less than reporting limit (lower limit of quantitation) for each element.

11.13.2 Run the CRI (LLCCV) solution right after the ICV and ICB, (or any other place at the beginning of the run after the ICV, ICB and before any real samples are analyzed). For the CRI, all elements of interest must be within 30% of the true value or within client specified limits.

11.14 Then analyze the CCV and CCB check standards. For the CCV, all elements to be reported must be within 10 percent of the true value and the replicates that are greater than 5 times the reporting limit should have a relative standard deviation of less than 5 percent. For the CCB, all elements to be reported must normally be less than the reporting limit (lower limit of quantitation). If either the CCV or CCB do not meet criteria, then elements failing this criteria must not reported in the area bracketed by this QC.

11.14.1 The internal standard levels in the CCV and CCB must also be within 30% of the internal standard level for the initial calibration. If they are outside of these levels, then no samples can be reported in the area bracketed by this QC.

11.15 After the initial QC is completed and before any samples are analyzed, the ICSA and ICSAB solutions must be analyzed. The method does not list specific criteria for the ICSA and ICSAB, but in house criteria will be applied. For all the spiked elements, the analyzed results must be within 20 percent of the true results. For unspiked elements, the interfering element solution should contain less than the absolute value of 3 times the reporting limit for each element. If these criteria are not met, then samples with significant interferences can not be reported until the instrument is optimized and the ICSA and ICSAB are within specifications.

11.15.1 If the run is longer than 12 hours, a second ICSA, ICSAB pair must be analyzed before the next 12 hours is started.

11.15.2 If mass changes are made for the analysis of an element, all QC criteria must be met for the new mass and it must be verified that appropriate correction factors are in place.

11.15.3 The Agilent 7700X includes collision/reaction cell technology. The instrument is tuned both in regular (non-cell) mode and in helium (collision/reaction) cell mode. This technology is used to minimize interferences during analysis. If this technology is not applied, then correction factors for interferences must be added into the method. Table 1B includes which elements are run using collision/reaction cell technology.

11.16 After the initial analytical quality control has been analyzed, the samples and the preparation batch quality control should be analyzed. Depending on the type of digestion and the sample matrix, samples and the associated QC should normally be diluted by a factor of from 2 to 5 before analysis. This dilution factor should be indicated in the sample ID file on the instrument.

11.16.1 Each sample analysis must be a minimum of 3 integrations. For samples containing levels of elements greater than approximately 5 times the reporting limits, the relative standard deviations for the replicates should be less than 10%. If not, reanalyze the sample. If, upon reanalysis, the RSDs are acceptable, then report the data from the reanalysis. If RSD's are not acceptable on reanalysis, then the results for that element may, on the reviewer's discretion, be footnoted that there are possible analytical problems indicated by a high RSD between replicates. In some cases, an additional dilution analysis may be needed. Check with the area supervisor or manager for additional information.

11.16.2 The internal standard levels must be monitored for all samples and quality control. If the internal standard is not within 30% of the internal standard level for the initial calibration blank, then the sample must be diluted by a factor of 5 to bring the internal standard to within the correct range. If the internal standard is still outside of the range after the initial 1:5 dilution, then additional dilutions must be done until the internal standard is within the appropriate range.

11.16.2.1 If an internal standard is present in a sample, then do not use that internal standard. For example, Y is sometimes seen in real samples. If the Y recoveries are high relative to the other internal standards, then do not use the Y internal standard.

11.16.3 For any readings that exceed the linear range for a given element, a dilution is required. After a high reading, the sample following the high one must be examined for possible carryover. A verification may be necessary by rinsing the lines with an acid solution and then rereading the sample.

11.16.4 Indicate dilution factors for samples using df followed by the dilution factor after the sample ID. There should be a space between the sample number and the df.

11.17 Between each sample, flush the nebulizer and solution uptake system with a blank rinse solution for a minimum of 30 seconds or for the required period of time to ensure that analyte memory effects are not occurring. (60 seconds is recommended for normal methods excluding Hg and B. Longer times may be needed when Hg and B are being analyzed.)

11.18 Analyze the continuing calibration verification solution and the continuing calibration blank after every ten samples and at the end of the sample run.

11.18.1 For the CCV, all elements to be reported must be within 10 percent of the true value and the replicates that are greater than 5 times the reporting limit should have a relative standard deviation of less than 5 percent. If the CCV solution is not within 10 percent of the true value, no samples can be reported in the area bracketed by the failing CCV for the failing element.

11.18.2 For the CCB, all elements to be reported must be less than the reporting limit (lower limit of quantitation).

11.18.3 The internal standard levels in the CCV and CCB must also be within 30% of the internal standard level for the initial calibration. If they are outside of these levels, then no samples can be reported in the area bracketed by this QC.

11.19 The CRI (LLCV) must be analyzed at the end of each calibration (analysis) batch. The acceptance criterion for the CRI check is 70 to 130% recovery. If an element does not meet this criterion, then all samples for that element in the concentration range between the CRI and the CCV must be reanalyzed. Samples containing concentrations higher than the CCV may be reported as long as CCV criteria are met.

11.19.1 More frequent CRI (LCCV) checks may be analyzed during the course of the run if system stability at the low end of the calibration is questionable or if the lab wants to ensure that fewer samples will have to be submitted for reanalysis if there is a failed CRI at the end of a run.

11.19.2 It is recommended that the CRI check be run bracketing every 4 to 8 hour period of analysis. It may be run as frequently as every 10 samples if the supervisory staff deems that this is necessary.

11.20 After the run is completed, convert the data file to a CSV format using the option on the results screen. First save the file on the local drive using the file naming system described below. Update the run in the LIMS and enter the run name into the workgroup using lower case characters. Then copy the data from the local drive to the LIMS drive.

11.20.1 The file should be named as followed- initial instrument indicator (X), date (MMDD), year, run type (soil, water, or mixed), and sequential run number for that day. For example, the first water run from 12/17/02 would be designated X121702w1.csv.

11.21 Calculations are done in the LIMS using the calculations shown below.

11.21.1 Calculation for aqueous samples.

original sample concentration of metal (µg/l) =

$$\frac{\text{(conc. in the digestate (µg/l)) x (final digestate volume (ml))}}{\text{(Initial sample volume (ml))}}$$

11.21.2 Calculation for solid samples.

original sample concentration of metal (mg/kg) =

$$\frac{\text{(conc. in the digestate (µg/l)) x (final digestate volume (ml))}}{\text{(Initial sample weight (g)) x (\%sol/100)}}$$

11.22 At the end of the analysis day the ICP-MS must be brought down using the following sequence.

- Rinse the tip in a solution of 1 percent nitric acid and .6 percent hydrochloric acid for 10 minutes and in DI water for 20 minutes. (Note: a stronger acid solution may be needed depending on the matrix of the samples that were analyzed.)
- Turn off the plasma using off button.
- Release the tension on the pump tubing.
- Turn off the cool flow and the printer.

12.0 QC REQUIREMENTS

12.1 This section outlines the QA/QC requirements necessary to meet the method 6020.

12.2 Instrument Detection Limits (IDLs). IDLs must be established for all analytes a minimum of once per quarter. They are calculated by taking the average of the standard deviations of three runs on three non-consecutive days from the analysis of a reagent blank solution with seven consecutive measurements per day.

12.3 LLQC (Lower Limit of Quantitation Check Sample) or LOQ Verification sample. A sample must be digested and analyzed initially and on an as needed basis to verify the quantitation limits for the method. Recoveries of this check must be within 70 to 130% of the true value. If recoveries are outside of this level, then the reporting limit must be increased to a level that can be verified.

12.3.1 For DOD work, the LOQ verification must be analyzed quarterly.

12.4 Method Detection Limits (MDLs). MDLs should be established for all analytes, using a solution spiked at approximately 2 to 5 times the estimated detection limit. To determine the MDL values, take seven replicate aliquots of the spiked sample and process through the entire analytical method. The MDL is calculated by multiplying the standard deviation of the replicate analyses by 3.14, which is the student's t value for a 99% confidence level. MDLs should be determined approximately once per year or whenever there is a significant change

in the background or instrument response. In general, if the amount spiked for the MDL is greater than 10 times the actual MDL, then the MDL should be redone with a lower spike level.

12.5 Linear Calibration ranges. The upper limit of the linear dynamic range needs to be established for each wavelength used by determining the signal responses from a minimum of three, preferably five, different concentration standards across the linear range. The linear calibration range which may be used for the analysis of samples should be judged by the analyst from the resulting data. The data, calculations and rationale for the choice of range made must be documented and kept on file. A standard at the upper limit must be prepared, analyzed and quantitated against the normal calibration curve. The calculated value should be within 10% (±10%) of the true value. Linear calibration ranges should be determined whenever there is a significant change in instrument response. They must be done at least every six months. For any readings that exceed the linear range for a given element, a dilution is required. In addition, if there significant interferences generated from elements above the linear range, than these elements must also be diluted so that accurate interfering element corrections can be applied. Normal linear range values by element are shown in Table 2.

12.6 Initial Calibration Verification (ICV) or Quality Control Sample (QCS) and Initial Calibration Blank (ICB). After every new calibration, an ICV must be analyzed. The analysis of the ICV may be followed by the analysis of the ICB, although this is not required by the method.

12.6.1 For the ICV, all elements to be reported must be within 10 percent of the true value and the replicates that exceed 5 times the reporting limit should have a relative standard deviation of less than 5 percent. The ICV must be from a different source than the calibration standards and must be near the mid-point of the calibration curve. If the ICV does not meet criteria, then the problem must be identified and corrected before samples can be run and reported for the element(s) that are outside of criteria. Correction of the problem can be verified by rerunning the check standard and showing that it meets QC criteria.

12.6.2 If an ICB is analyzed, than all elements to be reported must be less than the RL (LLOQ). If the ICB is outside of criteria, then the problem must be identified and corrected before samples can be run and reported for the element(s) that are outside of criteria. Correction of the problem can be verified by rerunning the check standard and showing that it meets QC criteria. Analysis of a CCB before running any reportable samples can be used to verify that the system meets calibration blank requirements.

12.7 Continuing Calibration Verification (CCV) and Continuing Calibration Blank (CCB). Analyze the continuing calibration verification solution and the continuing calibration blank after every tenth sample and at the end of the sample run.

12.7.1 For the CCV, all elements to be reported must be within 10 percent of the true value and the replicates that are greater than 5 times the reporting limit should have a relative standard deviation of less than 5 percent. The CCV should be made from the same source as the calibration standards at a concentration near the mid-level of the calibration curve. If an element does not meet the recovery criteria of the CCV, than no samples can be reported for that element in the area bracketed by the CCV.

12.7.2 For the CCB, all elements to be reported must be less than the reporting limit (LLOQ). If an element does not meet this criterion, then no samples can be reported for that element in the area bracketed by the CCB.

12.7.3 The internal standard levels in the CCV and CCB must also be within 30% of the internal standard level for the initial calibration. If they are outside of these levels, then no samples can be reported in the area bracketed by this QC.

12.8 Interference Check Standards. After the initial QC is completed and before any samples are analyzed, the ICSA and ICSAB solutions must be analyzed. The method does not give specific criteria for the ICSA and ICSAB, but in house criteria should be applied. For all the spiked elements, the analyzed results must be within 20 percent of the true results. For unspiked elements, the interfering element solution should contain less than the absolute value of 3 times the reporting limit for each element. If these criteria are not met, then samples with significant interferences can not be reported until the correction factors are optimized and the ICSA and ICSAB are within specifications.

12.8.1 If the run is longer than 12 hours, a second ICSA, ICSAB pair must be analyzed before the next 12 hours is started.

12.8.2 Both the ICSA and ICSAB solutions must be made fresh weekly.

12.8.3 If mass changes are made for the analysis of an element, all QC criteria must be met for the new mass and it must be verified that appropriate correction factors are in place.

12.9 Low Level Calibration Verification (CRI or LLCCV). The CRI standard containing the elements of interest at (or below) the reporting level for each element. The CRI (LLCV) must be analyzed at the beginning and end of each calibration (analysis) batch. The acceptance criterion for the CRI check is 70 to 130% recovery. If an element does not meet this criterion, then all bracketed samples for that element in the concentration range between the CRI and the CCV must be reanalyzed. Samples containing concentrations higher than the CCV may be reported as long as CCV criteria are met.

12.9.1 More frequent CRI (LCCV) checks may be analyzed during the course of the run if system stability at the low end of the calibration is questionable or if the lab wants to ensure that fewer samples will have to be submitted for reanalysis if there is a failed CRI at the end of a run.

12.9.2 It is recommended that the CRI check be run bracketing every 4 to 8 hour period of analysis. It may be run as frequently as every 10 samples if the supervisory staff deems that this is necessary.

12.10 Method Blank. The laboratory must digest and analyze a method blank with each set of samples. A minimum of one method blank is required for every 20 sample batch. If the method blank does not contain target analytes at a level that interferes with the project-specific DQOs, then the method blank is considered acceptable.

12.10.1 The default SOP limit for the method blank is that is must be less than one half of the reporting limit.

12.10.2 In addition, the blank is considered acceptable if it is less than 10% of the regulatory limit, or less than 10% of the lowest sample concentration for each analyte in a given preparation batch, whichever is greater.

12.10.3 If the method blank does not meet criteria, then it can be reanalyzed along with any associated samples. If it is still unacceptable, then all associated samples must be redigested and reanalyzed along with the other appropriate batch QC samples.

12.11 Lab Control Sample or Spike Blank. The laboratory must digest and analyze a laboratory control sample or spike blank with each set of samples. A minimum of one lab control sample or spike blank is required for every 20 sample batch. The laboratory should assess laboratory performance of the lab control and spike blank against recovery limits of 80 to 120 percent. In house lab control and spike blank limits may also be generated to support these default limits. If the lab control or spike blank is outside of the control limits for a given element, all samples must be redigested and reanalyzed for that element.

12.11.1 If solid lab controls are used, then the manufacturer's limits should be applied.

12.12 Matrix Spike. The laboratory must add a known amount of each analyte to a minimum of 1 in 20 samples. The matrix spike recovery is calculated as shown below. Recoveries should be assessed against default limits of 75 to 125 percent. In house limits may be generated for this method for informational purposes only. If a matrix spike is out of control, then the results should be flagged with the appropriate footnote and it is recommended that a post-digest spike be analyzed for the out of control element(s). If the matrix spike amount is less than one fourth of the sample amount, then the sample cannot be assessed against the control limits and should be footnoted to that effect. Note: Both the matrix spike amount and the sample amount are calculated to the IDL for any given element. Any value less than the IDL is treated as zero.

((Spiked Sample Result - Sample Result) / Amount Spiked) x 100 = matrix spike recovery

12.12.1 If a post-digest spike is required, the sample should be spiked with approximately 2 times the sample level or two times the reporting limits, whichever is greater. Limits of 80 to 120 percent are normally applied. The serial dilution is used to confirm any matrix effects. The post-digest spike recovery must be footnoted on the matrix spike recovery or otherwise noted in the quality control summary report.

12.13 Matrix Spike Duplicate (MSD) or Matrix duplicate (DUP). The laboratory must digest a matrix spike duplicate or matrix duplicate sample for a minimum of 1 in 20 samples. The relative percent difference (rpd) between the MSD and the MS or between the DUP and the sample should be assessed. The rpd is calculated as shown below. The control limit for the duplicate rpd is method defined as 20%. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of $\pm$ the reporting limit, then the duplicate is considered to be in control. Note: Both the duplicate amount and the sample amount are calculated to the IDL for any given element. Any value less than the IDL is treated as zero.

12.13.1 If a MSD or duplicate is out of control, then the data should be checked carefully to confirm that the high rpd for a given element is not a result of an analytical problem. If an analytical problem is suspected, the MSD or duplicate must be reanalyzed for confirmation. If the initial and reanalysis are in agreement (within 20%), then the high rpd is a result of preparation or sample issues and further analysis of the initial preparation is not required. If the initial and reanalysis are not in agreement due to an analytical problem, then any affected samples in the associated batch should also be reanalyzed for that element.

12.13.2 If more than 50% of the elements in a sample (that have levels of at least 5 times the reporting limit) have a high RPD, then the MSD or duplicate should be redigested for confirmation, unless the sample matrix is such that the non-homogeneity of the sample is visually apparent. If the results confirm, the results from the original MSD or duplicate should be flagged as indicative of possible sample non-homogeneity. If the results do not confirm, then the whole batch should be digested and reanalyzed.

12.13.3 If 50% or less of the elements in a sample (that have levels of at least 5 times the reporting limit) have a high rpd, then the high rpd(s) should be footnoted as indicating possible sample non-homogeneity unless other problems are suspected. If problems are suspected, the reviewer will initiate redigestion and reanalysis of the batch.

12.13.4 The calculations used to calculate RPD are shown below.

$$\frac{(|\text{MS Result} - \text{MSD Result}|) \times 100}{(\text{MS Result} + \text{MSD Result})/2} = \text{MSD RPD}$$

$$\frac{(|\text{Sample Result} - \text{Duplicate Result}|) \times 100}{(\text{Sample Result} + \text{Duplicate Result})/2} = \text{Duplicate RPD}$$

12.14 Serial Dilution. A serial dilution is required on a frequency of one in 20 samples. It is normally done on the same sample as is used for the matrix spike. If the analyte concentration is within the linear dynamic range of the instrument and sufficiently high (minimally a factor of at least 100 times greater than the concentration in the reagent blank), then an analysis of a fivefold (1+4) dilution must agree to within ± 10% of the original determination. If not, an interference effect must be suspected and the serial dilution result for the element with the suspected interference must be footnoted. The serial dilution is calculated as shown below.

$$\frac{100 \times ((\text{Sample result} - \text{Serial dilution result}))}{\text{Sample result}} = \text{Serial dilution percent difference}$$

12.14.1 Results of less than the IDL are treated as 0. The concentration in the reagent blank is normally < 3 times the IDL, so the factor of 100 times the concentration in the reagent blank (listed above) so the limits should be applied to sample concentrations of greater than 300 times the IDL.

12.15 Lower Limit of Quantitation check sample (LLQC). The LLQC is a sample at the reporting limit that is taken through the entire preparation and analytical process. This standard must be analyzed when reporting limits are initial established and on an as needed basis after that. The LLQC is equivalent to the LOQ (Limit of quantitation) standard which must be analyzed quarterly for the DOD QSM 4.1 program. The limits of quantitation are verified when all analytes in the LLQC sample are detected within 30% of their true value. If the limits cannot be verified at the spiked level, then the quantitation limit must be adjusted to a level where verification is successful.

13.0 DOCUMENTATION REQUIREMENTS

13.1 If samples or QC checks require reanalysis, a brief explanation of the reason must be documented on the run log. All instrument data should be exported to the LIMS system.

13.2 The Standard Preparation Logbook must be completed for all standard preparations. All information requested must be completed. The Accutest Lot Number must be cross-referenced on the standard vial.

13.3 The Instrument Maintenance Logbook must be completed when any type of maintenance is performed on the instrument. Each instrument has a separate log.

13.4 The correction factors from each method must be printed out each time a change is made and stored in a notebook in the lab. Each time the correction factors are modified, a new printout must be obtained.

13.5 Any corrections to laboratory data must be done using a single line through the error. The initials of the person and date of correction must appear next to the correction.

13.6 Supervisory (or peer) personnel must routinely review (approximately once per month) all laboratory logbooks to ensure that information is being recorded properly. Additionally, the

maintenance of the logbooks and the accuracy of the recorded information should also be verified during this review.

14.0 INSTRUMENT MAINTENANCE

14.1 Recommended periodic maintenance includes the items outlined below.

14.2 Change the pump tubing weekly or as needed.

14.3 Clean the nebulizer, torch, and injector tube every two to four weeks or more often as needed.

14.4 Change the sampler tip as needed (every one to two months).

14.5 Clean the recirculating pump lines as needed.

14.6 Clean the slides on the autosampler once per day.

15.0 POLLUTION PREVENTION & WASTE MANAGEMENT

15.1 Users of this method must perform all procedural steps in a manner that controls the creation and/or escape of wastes or hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids or solids to the environment must be followed. All method users must be familiar with the waste management practices described in section 15.2

15.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the waste management SOP, EHS004. This document describes the proper disposal of all waste materials generated during the testing of samples as follows:

15.2.1 Non hazardous aqueous wastes.

15.2.2 Hazardous aqueous wastes

15.2.3 Chlorinated organic solvents

15.2.4 Non-chlorinated organic solvents

15.2.5 Hazardous solid wastes

15.2.6 Non-hazardous solid wastes

16.0 ADDITIONAL REFERENCES

16.1 Refer to other SOP's for ICP-MS analysis (EPA 200.8).

TABLE 1A: ELEMENTS, MASSES, AND REPORTING LIMIT FOR THE THERMO ICP-MS

Mass and Element	Listed for analysis in 6020	Additional lines to monitor	CRI (LOQLL) CRI Check	Normal Digested Aqueous Sample Reporting Limit (Dilution Factor of 2) in ug/l.	Normal Digested Solid Sample Reporting Limit (Dilution Factor of 5) in mg/kg.	Comments
9Be	**		.5	1	.25	
11B		10B	5	10	2.5	
23Na			250	500	125	
25Mg		26Mg	250	500	125	24Mg has possible interferences from C-C
27Al	**		50	100	25	
39K			250	500	125	
43Ca		44Ca	250	500	125	44Ca has possible interferences from CO2
47Ti			1	2	0.5	
51V			4	8	2	
52Cr	**	53Cr	4	8	2	
55Mn	**		.5	1	0.25	
57Fe		56e	50	100	25	
59Co	**		.5	1	0.25	
60Ni	**	62Ni	4	8	2	
65Cu	**	63Cu	4	8	2	63 is the method recommended line, but 65 is used instead. 63Cu has possible interferences from ArNa
66Zn	**	67Zn, 68Zn	4	8	2	
75As	**		1	2	0.5	
82Se	**	77Se, 78Se	1	2	5	78Se used for correction only.
88Sr			1	2	0.5	
95Mo		97Mo, 98Mo	1	2	0.5	98Mo is the method recommended line, but 95 is used instead. 98Mo has possible interferences from ruthenium.
107Ag	**	109Ag	2	4	1	
111Cd	**	106Cd, 108Cd, 114 Cd	.5	1	0.25	
118Sn			1	5	NA	
121Sb	**	123Sb	.5	1	0.25	123Sb is the method recommended line, but 121Sb is used instead. Xe is a possible interference for 123Sb and is sometimes found as a contaminant in argon.
137Ba	**		1	2	0.5	
205Tl	**	203Tl	.5	1	0.25	
208Pb	**	206Pb,207Pb, and 208Pb summed and reported under 208Pb	.5	1	0.25	
13C, 53ClO, 77ArCl and 153BaO also included in method to monitor and correct for interferences.						

16.2 TABLE 1B: ELEMENTS, MASSES, AND REPORTING LIMIT FOR THE AGILENT ICP-MS

Mass and Element	Associated Tune (1 = no gas, 2= helium, 3= optimized helium)	Listed for analysis in 6020	Additional lines to monitor with associated tune	CRI (LOQLL) CRI Check	Normal Digested Aqueous Sample Reporting Limit (Dilution Factor of 2) in ug/l.	Normal Digested Solid Sample Reporting Limit (Dilution Factor of 5) in mg/kg.	Comments
9Be	1	**		.5	1	.25	
11B	1		10B – 1	5	10	2.5	
23Na	1		23Na – 2	250	500	125	
24Mg	1		24Mg – 2	250	500	125	
27Al	1	**	27Al – 2	25	50	25	
39K	1		39K – 2	250	500	125	
44Ca	1		43Ca – 1,2, 44Ca – 2	250	500	125	
47Ti	1		47Ti – 2	1	2	0.5	
51V	2		51V - 3	1	2	1	
52Cr	2	**		1	2	1	
55Mn	2	**		.5	1	0.25	
56Fe	2			25	50	25	
59Co	2	**		.5	1	0.25	
60Ni	2	**		1	2	1	
63Cu	2	**	65Cu – 2	1	2	1	
66Zn	2	**		2	4	2	
75As	2	**		0.5	1	0.25	
78Se	3	**	78Se – 2	0.5	1	.25	
88Sr	1			5	10	2.5	
95Mo	1			1	2	0.5	98Mo is the method recommended line, but 95 is used instead. 98Mo has possible interferences from ruthenium.
107Ag	1	**		.5	1	.25	
111Cd	1	**		.5	1	0.25	
118Sn	1			5	10	2.5	
121Sb	1	**		.5	1	0.25	123Sb is the method recommended line, but 121Sb is used instead. Xe is a possible interference for 123Sb and is sometimes found as a contaminant in argon.
137Ba	1	**		1	2	0.5	
205Tl	1	**		.5	1	0.25	
208Pb	1	**	206Pb,207Pb, and 208Pb summed and reported under 208Pb	.5	1	0.25	

TABLE 2A: RECOMMENDED STANDARDS AND ICV AND CCV LEVELS AND NORMAL LINEAR RANGES FOR **THERMO ICP-MS**

Mass and Element	STDA	STDB	STDC	STDD	STDE	STDF	STDG	STDI	NORMAL LINEAR RANGE		ICV	CCV
7Li	0	0.5	5	25	50	100	0	0	500		60	50
9Be	0	0.5	5	25	50	100	0	0	250		60	50
11B	0	0.5	5	25	50	100	0	0	250		60	50
23Na	0	0.5	5	25	50	100	5000	10000	100000		5500	5000
25Mg	0	0.5	5	25	50	100	5000	10000	100000		5500	5000
27Al	0	0.5	5	25	50	100	5000	10000	100000		5500	5000
39K	0	0.5	5	25	50	100	5000	10000	100000		5500	5000
43Ca	0	0.5	5	25	50	100	5000	10000	100000		5500	5000
47Ti	0	0.5	5	25	50	100	250	0	500		100	125
51V	0	0.5	5	25	50	100	0	0	500		60	50
52Cr	0	0.5	5	25	50	100	0	0	500		60	50
55Mn	0	0.5	5	25	50	100	0	0	500		60	50
57Fe	0	0.5	5	25	50	100	5000	10000	100000		5500	5000
59Co	0	0.5	5	25	50	100	0	0	500		60	50
60Ni	0	0.5	5	25	50	100	0	0	500		60	50
65Cu	0	0.5	5	25	50	100	0	0	500		60	50
66Zn	0	0.5	5	25	50	100	0	0	500		60	50
75As	0	0.5	5	25	50	100	0	0	500		60	50
82Se	0	0.5	5	25	50	100	0	0	500		60	50
88Sr	0	0.5	5	25	50	100	250	0	500		60	50
95Mo	0	0.5	5	25	50	100	0	0	500		100	125
107Ag	0	0.5	5	25	50	100	0	0	500		60	50
111Cd	0	0.5	5	25	50	100	0	0	500		60	50
118Sn	0	0.5	5	25	50	100	0	0	500		60	50
121Sb	0	0.5	5	25	50	100	0	0	500		60	50
137Ba	0	0.5	5	25	50	100	0	0	500		60	50
205Tl	0	0.5	5	25	50	100	0	0	500		60	50
208Pb	0	0.5	5	25	50	100	0	0	500		60	50
238U	0	0.5	5	25	50	100	0	0	500		60	50

TABLE 2B: RECOMMENDED STANDARDS AND ICV AND CCV LEVELS AND NORMAL LINEAR RANGES FOR **AGILENT ICP-MS**

Mass and Element	STDA	STDB	STDC	STDD	STDE	STDF	STDG	STDH	STDI	NORMAL LINEAR RANGE	ICV	CCV
6Li	0	0.5	5	25	50	100				500	60	50
9Be	0	0.5	5	25	50	100				500	60	50
11B	0	NA	5	25	50	100				500	60	50
23Na	0	NA	NA	NA	NA	100	1000	5000	10000	100000	5500	5000
24Mg	0	NA	NA	NA	NA	100	1000	5000	10000	100000	5500	5000
27Al	0	NA	NA	25	50	100	1000	5000	10000	100000	5500	5000
39K	0	NA	NA	NA	NA	100	1000	5000	10000	100000	5500	5000
44Ca	0	NA	NA	NA	NA	100	1000	5000	10000	100000	5500	5000
47Ti	0	1	5	25	50	100				500	60	50
51V	0	1	5	25	50	100				500	60	50
52Cr	0	1	5	25	50	100				500	60	50
55Mn	0	.5	5	25	50	100				500	60	50
56Fe	0	NA	NA	25	50	100	1000	5000	10000	100000	5500	5000
59Co	0	0.5	5	25	50	100				500	60	50
60Ni	0	1	5	25	50	100				500	60	50
63Cu	0	1	5	25	50	100				500	60	50
66Zn	0	2	5	25	50	100				500	60	50
75As	0	0.5	5	25	50	100				500	60	50
78Se	0	0.5	5	25	50	100				500	60	50
88Sr	0	NA	5	25	50	100				500	60	50
95Mo	0	1	5	25	50	100				500	60	50
107Ag	0	0.5	5	25	50	100				500	60	50
111Cd	0	0.5	5	25	50	100				500	60	50
118Sn	0	NA	5	25	50	100				500	60	50
121Sb	0	0.5	5	25	50	100				500	60	50
137Ba	0	1	5	25	50	100				500	60	50
205Tl	0	0.5	5	25	50	100				500	60	50
208Pb	0	0.5	5	25	50	100				500	60	50

TABLE 3: INTERNAL STANDARD MASSES AND ELEMENTS

Mass and Element	Associated Tune for Aglient only (1 = no gas, 2= helium, 3= optimized helium)	Comments
6Li	1	
45Sc	2	
72Ge	2, 3	(for Aglient only)
89Y	2, 3	Sometimes found in soil matrices. Monitor recoveries with other internal standards (for Thermo only)
103Rh	1, 2	
115In	1	
159Tb	1	
165Ho	1	
209Bi	1	

TABLE 4: MS AND BLANK SPIKE CONCENTRATIONS

Element	Soils Final Concentration in mg/kg	Mid -level Aqueous Final Concentration in µg/l	Low-level Aqueous Final Concentration in µg/l
Ag	10	50	100
Al	5400	2000	100
As	400	2000	100
B	100	2000	100
Ba	400	2000	100
Be	10	50	100
Ca	1250	25000	100
Cd	10	50	100
Co	100	500	100
Cr	40	200	100
Cu	50	250	100
Fe	5200	1000	100
K	1250	25000	100
Mg	1250	25000	100
Mn	100	500	100
Mo	100	2000	100
Na	1250	25000	100
Ni	100	500	100
Pb	100	500	100
Sb	100	500	100
Se	400	2000	200
Tl	400	2000	100
V	100	500	100
Zn	100	500	100
Sn	100	2000	100
Sr	100	2000	100
Ti	100	2000	100
Pd	100	2000	100

Lab Manager Wendy Jones

QA Manager Ad Ale

Effective Date: 8/7/13

TEST NAME: METALS BY INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY (ICP) USING SOLID STATE ICP.

METHOD REF: SW846 6010C

Revised Sections: ***Section 9.5.3, 12.17, should to must***
Additions: ***10.7.2.1.1***

1.0 SCOPE AND APPLICATION

1.1 This method is applicable for the determination of metals in water, wipes, sludges, sediments, and soils. Sample matrices are pretreated following SW846 methods for digestion of soil, sediment, sludge, wipe or water samples. Refer to specific digestion SOP's for more information on digestion techniques.

1.2 A variety of metals can be analyzed by ICAP. These include, but are not limited to, Al, Sb, As, Ba, Be, B, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, K, S, Se, Si, Ag, Na, Sr, Tl, Sn, Ti, Pd, V, W, Zn, and Zr.

2.0 SUMMARY

2.1 Prior to analysis, samples must be solubilized or digested using appropriate Sample Preparation Methods. When analyzing groundwater samples for dissolved constituents, acid digestion is not necessary if the samples are filtered and acid preserved prior to analysis.

2.2 This SOP describes operation of the ICAP 6500 Spectrometer following method SW846 6010C.

2.2.1 This inductively coupled argon plasma optical emission spectrometers (ICP-OES) uses an Echelle optical design and a Charge Injection Device (CID) solid-state detector to provide elemental analysis. Control of the spectrometer is provided by PC based iTEVA software.

2.2.2 In the instrument, samples are nebulized and the resulting aerosol is transported to the plasma torch. Element-specific emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a spectrometer, and the intensities of the emission lines are monitored the solid state detector.

2.2.3 Background correction is required for trace element determination. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background-intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. In one mode of analysis the position used should be as free as possible from spectral interference and should reflect the same change in

background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. Interferences which cannot be addressed with background correction must be corrected using the appropriate interelement correction factors.

3.0 REPORTING LIMIT AND METHOD DETECTION LIMIT

3.1 Reporting Limit. The normal reporting limits for this method have been established at the concentrations listed in Table 1. Reporting limits may vary depending on client needs and lab protocols, but the reporting limits must always be verified with a low check which meets the criteria outlined in this SOP. In addition, the reporting limits must always be greater than the MDL. Refer to the scheduling sheets and check with the metals supervisor for further information.

3.2 Method Detection Limit. Experimentally determine MDLs using the procedure specified in 40 CFR, Part 136, Appendix B. This value represents the lowest reportable concentration of an individual compound that meets the method qualitative identification criteria.

3.2.1 Experimental MDLs must be determined annually for this method.

4.0 DEFINITIONS

BATCH: A group of samples which behave similarly with respect to the sampling or the testing procedures being employed and which are processed as a unit. For QC purposes, if the number of samples in a group is greater than 20, then each group of 20 samples or less will all be handled as a separate batch.

CALIBRATION CHECK STANDARD. The calibration check standard is a mid-range calibration standard. It is recommended that the calibration check standard be run at a frequency of approximately 10 percent during an analysis run, whichever is more frequent, and at the end of the analysis sequence. For this method, the mid-level calibration check standard criteria is $\pm$ 10 percent of the true value and the relative standard deviation for the replicates that are greater than 5 times the reporting limit is less than 5 percent. The exception to this rule is if the recovery on the calibration check standard is high and the samples to be reported are less than the reporting limit.

EXTERNAL CHECK STANDARD. The external check standard is a standard from a separate source than the calibration curve that is used to verify the accuracy of the calibration standards. An external check must be run with each calibration. For this method, the external check standard criteria is $\pm$ 10 percent of the true value and the replicates that are greater than 5 times the reporting limit must have a relative standard deviation of less than 5 percent. If the external check is outside of the control limits for a given parameter, all samples must be reanalyzed for that parameter after the problem has been resolved.

SPIKE BLANK OR LAB CONTROL SAMPLE. Digest and analyze a laboratory control sample or spike blank with each set of samples. A minimum of one lab control sample or spike blank is required for every 20 samples. For a running batch, a new lab control sample or spike blank is required for each different digestion day. Assess laboratory performance against the control limits of 80 to 120 percent. In house limits must also be generated once sufficient data (usually a minimum of 20 to 30 analyses) is available to support the default limits. For solid lab controls, the elements must be within the range given by the lab control supplier. If the lab control or spike blank

is outside of the control limits for a parameter, all samples must be redigested and reanalyzed for that parameter. The exception is if the lab control or spike blank recovery is high and the results of the samples to be reported are less than the reporting limit. In that case, the sample results can be reported with no flag.

MATRIX: The component or substrate (e.g., water, soil) which contains the analyte of interest.

MATRIX SPIKE DUPLICATE: A matrix spike duplicate sample is digested at a minimum of 1 in 20 samples. The relative percent difference (RPD) between the matrix spike duplicate and the matrix spike must be assessed. A duplicate may be used in place of the matrix spike duplicate on client request. The matrix spike duplicate RPD is calculated as shown below. The control limit for the duplicate is 20% rpd. If a duplicate is out of control, flag the results with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of ± the reporting limit, then the duplicate is considered to be in control.

$$\frac{(|\text{Matrix Spike Result} - \text{Matrix SpikeDuplicate Result}|) \times 100}{(\text{Matrix Spike Result} + \text{Matrix Spike Duplicate Result})/2} = \text{Duplicate RPD}$$

MATRIX SPIKE: The laboratory must add a known amount of each analyte to a minimum of 1 in 20 samples. The matrix spike recovery is calculated as shown below. Assess laboratory performance against the default limits of 75 to 125 percent. If a matrix spike is out of control, then the results must be flagged with the appropriate footnote. If the matrix spike amount is less than one fourth of the sample amount, then the sample cannot be assessed against the control limits and must be footnoted to that effect.

$$\frac{(\text{Spiked Sample Result} - \text{Sample Result}) \times 100}{(\text{Amount Spiked})} = \text{Matrix Spike Recovery}$$

METHOD BLANK. The laboratory must digest and analyze a method blank with each set of samples. A minimum of one method blank is required for every 20 samples. For a running batch, a new method blank is required for each different digestion day. If no digestion step is required, then the method blank is equivalent to the reagent blank. The method blank must contain the parameter of interest at levels of less than ½ of the reporting limit for that parameter. If the method blank contains levels over this level, then the samples must be redigested and reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the method blank level. In addition, if all the samples are less than a client required limit and the method blank is also less than that limit, then the results can be reported as less than that limit.

METHOD DETECTION LIMITS (MDLS). The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte. MDLs must be determined approximately once per year for frequently analyzed parameters.

REAGENT BLANK: The reagent blank is a blank that has the same matrix as the samples, i.e., all added reagents, but did not go through sample preparation procedures. The reagent blank is an indicator for contamination introduced during the analytical procedure. (Note: for methods requiring no preparation step, the reagent blank is equivalent to the method blank.) Either a reagent blank or a method blank must be analyzed with each batch of 20 samples or less. The concentration of the analyte of interest in the reagent blank must be less than the reporting limit for that analyte. If the reagent blank contains levels over the reporting limits, the samples must be reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the reagent

blank level. In addition, if all the samples are less than a client required limit and the reagent blank is also less than that limit, then the results can be reported as less than that limit.

REAGENT GRADE: Analytical reagent (AR) grade, ACS reagent grade, and reagent grade are synonymous terms for reagents which conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.

REAGENT WATER: Water that has been generated by any method which would achieve the performance specifications for ASTM Type II water.

STANDARD CURVE: A plot of concentrations of known analyte standards versus the instrument response to the analyte. Calibration standards are prepared by successively diluting a standard solution to produce working standards which cover the working range of the instrument. Standards must be prepared at the frequency specified in the appropriate section. The calibration standards must be prepared using the same type of acid or solvent and at the same concentration as will result in the samples following sample preparation. This is applicable to organic and inorganic chemical analysis.

LOW LEVEL CALIBRATION VERIFICATION (CRI or LLCCV). The LLCCV or CRI standard is a check standard containing the elements of interest at (or below) the reporting level for each element. For this method, the CRI (LLCV) must be analyzed at the beginning and end of each calibration (analysis) batch. The acceptance criterion for the CRI check is 70 to 130% recovery. If an element does not meet this criterion, then all bracketed samples for that element in the concentration range between the CRI and the CCV must be reanalyzed. Samples containing concentrations higher than the CCV may be reported as long as CCV criteria are met.

5.0 HEALTH & SAFETY

5.1 The analyst must follow normal safety procedures as outlined in the Accutest Health and Safety Plan and Personal Protection Policy, which include the use of safety glasses and lab coats. In addition, all acids are corrosive and must be handled with care. Flush spills with plenty of water. If acids contact any part of the body, flush with water and contact the supervisor.

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical must be treated as a potential health hazard. Exposure to these reagents must be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets must be made available to all personnel involved in these analyses.

6.0 PRESERVATION & HOLDING TIME

6.1 All water samples should be preserved with nitric acid to a pH of 2 or less. All solid samples must be stored in a refrigerator at 4 degrees C.

6.2 All samples should be analyzed within 6 months of the date of collection.

7.0 INTERFERENCES

7.1 Several types of interferences can cause inaccuracies in trace metals determinations by ICP. These interferences are discussed below.

7.2 Spectral interferences are caused by overlap of a spectral line from another element, unresolved overlap of molecular band spectra, background contribution from continuous or recombination phenomena, and background contribution from stray light from the line emission of high concentration elements. Corrections for these interferences can be made by using interfering element corrections, by choosing an alternate analytical line, and/or by applying background correction points.

7.3 Physical interferences can be caused by changes in sample viscosity or surface tension, by high acid content in a sample, or by high dissolved solids in a sample. These interferences can be reduced by using an internal standard, by making sample dilutions or by analyzing a sample using the method of standard additions.

7.4 Chemical interferences are not pronounced with ICAP due to the high temperature of the plasma, however if they are present, they can be reduced by optimizing the analytical conditions (i.e. power level, torch height, etc.).

8.0 EQUIPMENT AND SUPPLIES

8.1 Currently there are four solid state ICPs available for use in the lab. All are Thermo 6500 ICP units. These units have been optimized to obtain low detection limits for a wide range of elements. Since they are solid state systems, different lines may be included for elements to obtain the best analytical results. However, the lines which are normally included in the normal analysis program are shown in Table 2.

8.2 Instrument auto-samplers. For random access during sample analysis.

8.3 Class A volumetric glassware and pipets.

8.3.1 All glassware must be washed with soap and tap water and then soaked in a 10% nitric acid bath for a minimum of 2 hours. It must then be rinsed at least 3 times with deionized water.

8.4 Glass autosampler tubes

8.4.1 Autosampler tubes must be washed with soap and tap water and then soaked in a 10% nitric acid bath for a minimum of 2 hours. They must then be rinsed at least 3 times with deionized water.

8.5 Autopipeters with tips. These must be calibrated and checked as outlined in the autopipeter SOP, EQA004.

9.0 REAGENTS

9.1 All chemicals listed below are reagent grade unless otherwise specified. Deionized water must be used whenever water is required. The expiration date for standards and reagents is the date supplied by the manufacturer or if no expiration date is given, a default of 6 months is used. For

acid solutions (nitric, sulfuric, hydrochloric) the expiration date is 2 years from the date of preparation of the solution.

9.2 Hydrochloric acid, trace metals grade.

9.3 Nitric Acid, Baker instra-analyzed or equivalent.

9.4 Standard stock solutions available from Absolute, Inorganic Ventures, MV Laboratories, Ultra Scientific or equivalent. Note: All standards must be ICP quality standards.

9.5 Calibration Standards. These can be made up by diluting the stock solutions to the appropriate concentrations . It is recommended that fresh calibration standards must be prepared a minimum of every two weeks. They must be monitored on a daily basis by comparison to an ICV. Standards which are going to be stored for several days must be transferred to FEP fluorocarbon or previously unused polyethylene or polypropylene bottles for long term storage.

9.5.1 Standards must be approximately matrix matched to the samples. For most samples, a 5 percent nitric acid and 5 percent hydrochloric acid will approximate the acid matrix of the sample and limit nebulization problems. If it is known that the samples contain a significantly different acid matrix, then the matrix of the standards must be modified or the samples must be diluted so that they are in a similar matrix to the curve.

9.5.2 Standards must be prepared so that there is minimal spectral interference between analytes.

9.5.3 Refer to the standards book for the make-up and concentrations of standards and stock solutions being used to calibrate the ICP. The standard curve consists of a blank and 1 non-zero standards at the levels shown in Table 3.

9.6 Calibration/Rinse Blank. The calibration blank is prepared by diluting a mixture of 50 ml of concentrated nitric acid and 50 ml of concentrated hydrochloric acid to a final volume of 1 liter with deionized water.

9.7 Analytical Quality Control Solutions. All of the solutions below are prepared by adding either mixed or single element metals solutions to a solution containing 5 percent nitric acid and 5 percent hydrochloric acid and diluting to a fixed final volume with this acid mixture. All of these solutions must be placed in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles for long term storage.

9.7.1 Initial Calibration Verification solution. This standard solution must be made from a different source than the calibration curve. The values for each element must be near the midpoint of the calibration curve. This solution is used to verify the accuracy of the initial calibration. See Table 4 for suggested ICV concentrations.

9.7.2 Continuing Calibration Verification solution. The metals concentrations for this standard must be at approximately the mid-point of the calibration curve for each element. This standard must be prepared from the same source that is used for the calibration curve. See Table 4 for suggested CCV concentrations.

9.7.3 Interference Element Check Solutions. These solutions must be used on a periodic basis to check the interfering element corrections on the instruments. Note: If

interferences from different elements than those listed below are a problem, the interfering element solutions may be modified. Two acceptable solutions are outlined below.

9.7.1.1 ICSA Solution. The ICSA solution contains only the interfering elements. The recommended concentrations are shown below. If the linear ranges on a given instrument are lower than these levels, the concentrations may be set near the top of the linear range for those elements.

Al	500 mg/L
Ca	400 mg/L
Fe	200 mg/L
Mg	500 mg/L

9.7.1.2 ICSAB Solution. The ICSAB solution contains both the interferents and the analytes of interest. The recommended concentrations are shown below. If the linear ranges on a given instrument are lower than these levels, the concentrations may be set near the top of the linear range for those elements

Ag	1.0 mg/L	Zn	1.0 mg/L
Ba	0.50 mg/L	As	1.0 mg/L
Be	0.50 mg/L	Se	1.0 mg/L
Cd	1.0 mg/L	Sb	1.0 mg/L
Co	0.50 mg/L	Tl	1.0 mg/L
Cr	0.50 mg/L	Mo	0.5 mg/L
Cu	0.50 mg/L	Pd	0.5 mg/L
Mn	0.50 mg/L	Al	500 mg/L
Ni	1.0 mg/L	Ca	400 mg/L
Pb	1.0 mg/L	Fe	200 mg/L
V	0.50 mg/L	Mg	500 mg/L
W	0.50 mg/L	Zr	0.50 mg/L
Li	0.50 mg/l	Sr	0.5 mg/l
Bi	0.50 mg/l	Ti	0.5 mg/l
B	0.50 mg/l	S	0.5 mg/l
Sn	0.50 mg/l	Si	0.5 mg/l

9.7.2 CRI Standards (also referred to as LLCCV). The CRI standard must contain the elements of interest at (or below) the reporting limit for each element. The CRI level is at the reporting limit as shown in Table 1. This must be prepared by diluting calibration standard(s) to the reporting limit level for each element. They must be made in the same matrix as the calibration standards. Note: The CRI must be verified at the RL before any dilutions are applied

9.8 Matrix Spike and Spike Blank Solution (For soil samples). The final concentrations suggested for the matrix spike and spike blank solutions are shown in Table 5. The spiking solution is prepared by adding either mixed or single element metals solutions to a solution containing 2 percent nitric acid and diluting to a fixed final volume with this acid mixture. Two mls of this stock solution must be added to the spike blank and the matrix spike before they are digested and brought to a final volume of 100 ml.

9.9 Matrix Spike and Lab Control Solution (For aqueous samples and TCLP leachates).

9.9.1 The final concentrations suggested for the matrix spike are shown in Table 5. Two spiking solutions, which are used for aqueous samples and TCLP leachates respectively, are prepared by adding either mixed or single element metals solution to solutions containing 2 percent nitric acid and diluting to a fixed final volume with this acid mixture. 0.5 ml of the resulting stock solution is added to the matrix spike sample before they are digested.

9.9.2 A lab control sample must be digested and analyzed for every batch of 20 samples or less. The LCS is prepared by adding either mixed or single element metals solutions to DI water and bringing up to a fixed final volume. For TCLP samples, the lab control must be made using blank leachate solution rather than DI water. 50 ml of this solution is digested and brought to a final volume of 50 ml. In situations where any odd elements, such as B, Si, Sr, Sn, and Pd, is of interest for a specific project, besides a lab control, a spike blank is also digested.

9.10 Liquid Argon or Argon Gas. Argon is provided by Air Products in the large outdoor tank. No lab monitoring of the tank is normally necessary

9.11 Internal Standard Solution (with matrix modifier). To a 1 liter flask containing approximately 800 ml of DI water, add 20.0 ml of 10,000 mg/l Cesium solution, 5.0 ml of 10000 mg/l indium, and 1.000 ml of 10000 mg/l yttrium. Add 50 ml concentrated nitric acid and 50 ml concentrated hydrochloric acid and bring to a final volume of 1000 ml and mix well. This solution is added to all samples and standards as the instrument is running using a split line on the peristallic pump

10.0 PROCEDURE

10.1 General procedure on how to operate the SS Trace1 is described below. Refer to the Thermo 6500 operation manual for further details.

10.2 Before bringing up the instrument, make sure that the lines, the torch, the nebulizer, and the spray chamber are clean, the dehumidifier is filled with DI water up to the level between Minimum and Maximum, and that there are no leaks in the torch area.

10.3 Turn on the recirculating cooler. Verify that the liquid argon is turned on.

10.4 Set up the pump tubing and engage the peristaltic pump.

10.5 Put a new solution of acid rinse into the rinse reservoir. (Note: the composition of the rinse solution may be periodically changed to minimize sample introduction problems and sample carryover.) If internal standard is being used, make sure that sufficient internal standard solution is prepared.

10.6 Start up the instrument following the sequence shown below.

10.6.1 Double click the **iTEVA Control Center** Icon on desktop. Type ***admin*** in User Name field, and then click OK.

10.6.2 Once the iTEVA Control Center window is opened, click on **Plasma** Icon at status bar area. Then click on **Instrument Status** to check the interlock indicators (torch compartment, purge gas supply, plasma gas supply, water flow and exhaust must be in green; drain flow and busy must be in gray) and the Optics Temperature. (It should be around 38°C.) Click on the Close box.

10.6.3 Click **Plasma On**. When the plasma is on, click close. Let the instrument warm up for 15 to 20 minutes before starting the analysis. New tubing may take an hour to stabilize .

10.7 Torch Alignment and Auto Peak

10.7.1 If the torch has been cleaned, then it has to be realligned after it is replaced

10.7.1.1 Open the method and then click on **Sequence** tab, then click on List View Icon until you reach rack display.

10.7.1.2 Go to S-6 position (you can assign any position in the rack for torch alignment), then right click to select Go to empty sample S:6. (Now, the autosampler tip moves from Rinse to this position)

10.7.1.3 Click on **Analysis** tab, then select **Torch Alignment** from **Instrument** drop down menu. There will be a pop up dialog box present. Click RUN. Then there will be another dialog box pop up (This is a reminder for Torch Alignment Solution (2 ppm Zn)), click Ok. Now, the instrument is initiating an automated torch alignment. It takes about 7 minutes to complete this step. Progress is indicated in the progress bar.

10.7.1.4 After Torch Alignment is done, click Close. Click on **Sequence** tab, then follow by **List View** Icon.

10.7.1.5 Go to Rinse position at rack display, right click to select Go to rinse and let it rinse for 2 minutes.

10.7.2 Perform Auto Peak.

10.7.2.1 It is recommended that the Auto Peak Adjust procedure be performed monthly or whenever the peak shape has shifted for any element. A standard that contains all of the lines of interest is used and the system automatically makes the appropriate fine adjustment. (CCV solution is used for this process.)

10.7.2.1.1 A shift in peak shape can be defined as when the peak is no longer in the middle of the defined viewing window. The window must be set so that the peak is approximately centered and there is a sufficient area measured so that reproducible, consistent data can be obtained at reporting limit levels. This is done as part of the automatic process, but the window size can be adjusted manually in the method based on the shape of the peak to obtain the best fit for the peak. A wider peak may need a broader integration window for

the best analysis. In general, the window should cover at least the top 1/3 of the peak.

10.7.2.2 Click **Sequence** tab, then click on **List View** Icon till the rack is displayed.

10.7.2.3 Go to S-5 position (you can assign any position in the rack for auto peak adjust), then right click to select Go to empty sample S:5. (Now, the autosampler tip moves from Rinse to this position). Click on **Analysis** tab. All elements' result is showed in the display area. From **Instrument** drop down menu, select **Perform Auto Peak**. There will be a pop up dialog box present. Highlight _All Elements_, then click RUN. Then there will be another dialog box pop up (This is a reminder for Perform Auto Peak Solution), click Ok. Now, the instrument is performing auto peak adjust. It takes about 5 minutes to complete this process. The Auto Peak dialog box will show a green " √" in front of All Elements, which indicates Auto Peak is completed.

10.8 Open the method and start up the run.

10.8.1 Click on **Analyst** Icon at the workspace. Go the Method and choose Open from the drop down menu. Select the method with a Revision (usually select the last revision used).

10.8.2 Go to **Method** tab at the bottom of left-hand corner to click on **Automated Output** at the workspace area. Type a filename in Filename field in the data display area (i.e.: SA073107M1: starts with SA, then follow by MM-DD, then M1; M1 indicates the first analytical run for that day, then follow by M2, M3 and so on for the second and third runs).

10.8.3 Click on **Sequence** tab at the bottom of left-hand corner. From **Auto-Session** drop down menu bar, click on **New Autosampler** to create a sequence. This will pop up a dialog box , then click on **New** and fill number of samples (i.e.: 100) in the Number of Samples field and the sample ID (usually leave this field empty) in Sample Name field. Type a sequence name (i.e.: SEQ073107M1: starts with SEQ, then MM-DD-YY, then M1; M1 indicates the first analytical run for that day, then follow by M2, M3 and so on for the second and third runs) in the Sequence Name field. Click OK, then put in "0" on Settle Time Between Sequences box, click OK.

10.8.4 Right click on **Untitled** (CETAC ASX-520 Enviro 5 Named Rack is the rack that currently using) at the workspace area, click on **Auto-Locate ALL** to locate all samples.

10.8.5 Double click on **Untitled** again, then click on the sequence name (i.e.: SEQ073107M1), on the data display area, type the sequence in Samplename column, dilution factor (if needed) in CorrFact column, check the box in front of Check column, and select an appropriate check table.

10.8.6 Once done with creating sequence, go to **Method** drop down menu and save all changes as **Save As**. There will be a Save a Method dialog box present, go to Save

Option to check on "Overwrite Method and bump revision number" box, then click OK.

10.8.7 Go to **Sequence** tab, click on **List View** Icon from tool bar, then click on **Connect Autosampler to PC and Initialize** Icon. (Now, the autosampler tip is up and sits on the top of the rinse cup.)

10.8.8 The sequence includes the calibration and run quality control.

10.8.8.1 Calibrate the instrument as outlined below using the standards shown in Table 3. This calibration procedure is done a minimum of once every 24 hours. The calibration standards may be included in the autosampler program or they may be run separately.

10.8.8.2 Analyze ICV and ICB after the calibration is completed and before any samples are analyzed. An ICB may be run following the ICV, but is not required.)

10.8.8.2.1 For mixed runs (EPA 200.7 and SW846 6010C), the first CCV is designated the ICCV. For samples and quality control, insert the list pointer after a space after the sample. Check with the metals supervisors for additional information on the use of listpointers. In general, listpointer 2 refers to the SW846 6010 method and listpointer 1 refers to EPA 200.7 method.

10.8.8.3 Low Level Calibration Verification (Low checks or LLCCV)- Run low checks at reporting limits levels after ICCV and CCB. The low checks are named as CRI (or CRIB for DOD run), CRID and CRIA. The levels for each low check are listed in Table 8, Table 9 and Table 10.

10.8.8.3.1 Muti-level low check solutions must be analyzed for default reporting limits and special client reporting limits.

10.8.8.3.2 Low checks (LLCCV) must be analyzed at the end of each calibration (analysis) batch. The acceptance criterion for the CRI check is 70 to 130% recovery. If an element does not meet this criterion, then all samples for that element in the concentration range between the low checks and the CCV must be reanalyzed. Samples containing concentrations higher than the CCV may be reported as long as CCV criteria are met.

10.8.8.3.3 More frequent CRI (LCCV) checks may be analyzed during the course of the run if system stability at the low end of the calibration is questionable or if the lab wants to ensure that fewer samples will have to be submitted for reanalysis if there is a failed CRI at the end of a run.

10.8.8.3.4 It is recommended that the CRI check be run bracketing every 4 to 8 hour period of analysis. It may be run as frequently as every 10 samples if the supervisory staff deems that this is necessary

10.8.8.3.5 Method limits of 70 to 130% are applied to the low check standard, but tighter criteria may be needed in some client or project specific situations.

10.8.8.3.6 CRIB is only used for DOD runs and the limits are 80 to 120%.

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10.8.8.4 Before analyzing any real samples, an interference check solution must be checked. For all spiked elements, the analyzed results must be within 20 percent of the true results. For unspiked elements, the interfering element solutions must contain less than two times the absolute value of the reporting limit for each element.

10.8.8.5 If the interfering element solution is not within specifications and that element must be reported, then new interfering element correction (IEC) factors will need to be generated following the procedure outlined in Section 11 below. If new IEC's are generated, then the run must be restarted from the ICSA, ICSAB quality control samples and new CCV checks must be run before any samples can be reported.

10.8.8.6 After the initial analytical quality control has been analyzed, the samples and the preparation batch quality control must be analyzed. Each sample analysis must be a minimum of 2 readings using at least a 5 second integration time. For samples containing levels of elements greater than approximately 5 times the reporting limits, the relative standard deviations for the replicates must be less than 5%. If not, reanalyze the sample. If, upon reanalysis, the RSDs are acceptable, then report the data from the reanalysis. If RSD's are not acceptable on reanalysis, then the results for that element must be evaluated by the data reviewer and footnoted if necessary. In some cases, an additional dilution analysis may be needed. Check with the area supervisor or manager for additional information.

10.8.8.7 Between each sample, flush the nebulizer and solution uptake system with a blank rinse solution for the required period of time to ensure that analyte memory effects are not occurring. A time of 120 seconds is recommended for most analyses with the current autosampler set-up.

10.8.8.8 Analyze the continuing calibration verification solution and the continuing calibration blank after every tenth samples during an analysis run, whichever is more frequent, and at the end of the sample run.

10.8.8.9 If the CCV solution is not within 10 percent of the true value, no samples can be reported in the area bracketed by the failing CCV for the failing element. Additionally, for the elements with a CCV greater than 5 times the reporting limit, the relative standard deviation for the replicates must be less than 5 percent.

10.8.8.10 The CCB results must be less than the reporting limit or limit of quantitation for each desired target analyte. If this criterion is not met, then no samples

can be reported in the area bracketed by the failing CCB for the failing element and all samples must be submitted for reanalysis.

10.8.8.10.1 However, if the samples are high relative to the CCB (> 10 X the CCB level) and a higher reporting limit is acceptable for the final end use of the data, then the samples may be evaluated using a higher reporting limit to meet the CCB criteria. This must be clearly documented on the run if a higher reporting limit is applied.

10.8.8.10.2 In addition, at the reviewer's discretion, samples that are < RL may be reported when the CCB is biased high. Analysts must assume that samples bracketed by a failing CCB must be reanalyzed unless instructed otherwise.

10.8.8.10.3 If a CCB fails, if possible, the analyst must stop the run and run a new CCV, CCB pair before proceeding with the analysis of any additional samples.

10.8.8.11 For one sample per preparation batch, or whenever matrix interferences are suspected for a batch of samples, a serial dilution must be prepared. Normally the sample used for the serial dilution is the sample that is used for the matrix spike and matrix spike duplicate. For the serial dilution, a 1:5 dilution must be made on the sample. The results of the 1:5 dilution must agree within 10 percent of the true value as long as the sample is greater than 50 times the reporting limit for that element before dilution (or 10 times the reporting limit after dilution) and the sample results are within the linear range. If not, an interference effect must be suspected and the serial dilution result for the element with the suspected interference must be footnoted. The serial dilution is calculated as shown below

10.8.8.12 If the matrix spike or matrix spike duplicate is out of acceptable limits, then it is recommended that post-digest spikes be prepared to determine potential interferences. For the post-spike, the sample must be spiked with approximately 2 times the sample level or two times the reporting limits, whichever is greater. Limits of 80 to 120 percent are applied. The serial dilution is used to confirm any matrix effects. The post-digest spike recovery must be footnoted on the matrix spike recovery or otherwise noted in the quality control summary report.

10.8.8.13 For any readings that exceed the linear range for a given element, a dilution is required. After a high reading, the sample following the high one must be examined for possible carryover. A verification may be necessary by rinsing the lines with an acid solution and then rereading the sample. A limit check table may be built into the autosampler file so that samples exceeding the linear range are flagged on the raw data.

10.8.8.14 For the interelement spectral interference corrections to remain valid during sample analysis, the interferent concentration must not exceed its linear range. If the interferent exceeds its linear range or its correction factor is big enough to affect the element of interest even at a lower concentration, sample dilution with reagent blank and reanalysis is required. In these

circumstance analyte detection limits are raised. Check with metals supervisor for more information.

10.8.8.15 Anytime that the interference is large relative to the sample, dilution may be required. Check with the metals supervisor for more information.

10.8.8.16 For any readings where the internal standard is outside of the range of 70 to 130% of the internal standard level in the calibration blank, then the sample must be diluted until the internal standard is within that range.

10.8.9 This method does not require the analysis of an interfering element check solution at the end of the run. However, this may be required to meet other method and/or client requirements. Run the ICSA and ICSAB solutions as instructed by the metals lab supervisor or manager or as noted in the program code instructions.

10.8.10 After the instrument is optimized, click **Run Auto-Session** Icon to start the run.

10.8.11 If you need to add or delete samples once the run is started, follow the steps shown below.

10.8.11.1 Adding Samples.

10.8.11.1.1 Click on **Sequence** tab, then click on **List View** Icon at the tool bar. There is the sequence table on the data display area.

10.8.11.1.2 Click on **Add Samples** Icon. This will pop up the dialog box, then fill number of samples that need to add in field. Click OK. By doing this, samples will be added at the end of sequence without a location the rack.

10.8.11.1.3 Go to the added samples, on the to position ID column, assign a number for each sample. This number will be the position in the rack. On the Samplename column, type in sample IDs, fill in Corr Fact (if needed) and Check Table.

10.8.11.1.4 The added samples will be analyzed at the end of the original sequence run order unless you assign them to run under different order.

10.8.11.2 Deleting Samples.

10.8.11.2.1 Click on **Sequence** tab, then click on **List View** Icon under the sequence display area.

10.8.11.2.2 To the sample that need to be deleted, on the to position ID column, change the number to "0". By doing this, that sample will be unlocated in the rack and the autosampler tip will go to the next sample.

10.9 When the analysis is completed export the data to LIMS following the procedure outlined below.

10.9.1 Double click on **ePrint** Icon on desktop. There will be a LEADTOOLS ePRINT dialog box pop up, then click **Finish Jobs** and **OK** boxes.

10.9.2 Double click the **PDF** Icon on desktop, the PDF file will present as Document_#. Right click on that file, select **Rename** to change the file name to an assigned analytical run ID. (i.e.: MA8324). This is the raw data for MA8324.

10.9.3 Drop the raw data to Lims.

10.9.4 By completing above steps, the raw data (i.e: MA8324) can be pulled up in the Raw Data Search function.

10.10 The data must be reviewed in the LIMS as outlined in the inorganic data review SOP, EQA034. Calculations for water samples are done automatically in the LIMS using the equation shown below.

original sample concentration of metal (μg/l) =

$$\frac{\text{(conc. in the digestate (μg/l)) x (final digestate volume (ml))}}{\text{(Initial sample volume (ml))}}$$

10.11 Aft the end of the analysis day, the ICP must be brought down using the following sequence:

10.11.1 Place the autosampler tip in rinse cup and rinse in a mixed solution of 5% nitric acid and 5% hydrochloric acid for 10 minutes and in DI water for 20 minutes. **Note**: A stronger acid may be needed depending on the matrix of the samples that were analyzed.

10.11.2 Turn off the plasma by click on the **Plasma** Icon and click on **Plasma Off**.

10.11.3 Close all iTEVA programs/ windows.

10.11.4 Release the tension on the sample pump platen.

10.11.5 Switch off recirculating chiller.

11.0 PROCEDURE FOR GENERATION OF INTERFERING ELEMENT CORRECTION FACTORS

11.1 All IEC's must be verified and updated a minimum of once every 6 months or whenever instrument conditions change significantly. It is recommended that elements with frequent high concentrations or with large IEC's should be checked more frequently.

11.2 Calculate the IEC correction factors and enter them into the method. Verify that the recalculated sample results are within QC limits. Calculate the correction factor using the equation shown below. This correction factor must be added to the correction factor already in place in the method for a given element.

$$IEC = \frac{\text{Concentration Result of the element with the interference}}{\text{Concentration result of the interfering element}}$$

11.3 Analyze the ICSA/ICSAB solutions and/or SIE solutions and verify that the combined standards are within QC limits. If they are not, make additional changes to the IEC factors and then re-verify both the individual and combined solution values.

11.4 Save and update the method.

11.5 Interfering element correction factors saved as raw data along with the run printouts on a daily basis so that the IEC's for a given run are traceable.

12.0 QC REQUIREMENTS

12.1 This section outlines the minimum QA/QC operations necessary to satisfy the analytical requirements for method SW846 6010C.

12.2 Method Detection Limits (MDLs). MDLs must be established for all analytes, using a solution spiked at approximately 3 to 5 times the estimated detection limit. To determine the MDL values, take seven replicate aliquots of the spiked sample and process through the entire analytical method. The MDL is calculated by multiplying the standard deviation of the replicate analyses by 3.14, which is the student's t value for a 99% confidence level. MDLs must be determined approximately once per year or whenever there is a significant change in the background or instrument response.

12.3 Instrument Detection Limits (IDLs). Instrument Dection Limits (IDLs). It is required that IDL's be completed a minimum of every 3 months for all analytes or whenever instrument conditions have significantly changed. The Instrument Detection Limits (in ug/L) are determined by analyzing 7 replicates of a reagent blank solution on 3 non-consecutive days. The IDL is defined as 3 times the average of the standard deviations of the 3 days. For the IDL, each measurement shall be performed as though it were a separate analytical sample (i.e., each measurement shall be followed by a rinse and/or any other procedure normally performed between the analysis of separate samples). IDLs shall be determined and reported for each wavelength used in the analysis of the samples.

12.4 Linear Calibration ranges. The upper limit of the linear calibration ranges must be established for each analyte by determining the signal responses from a minimum of three concentration standards, one of which is close to the upper limit of the linear range. The linear calibration range which may be used for the analysis of samples must be judged by the analyst from the resulting data. Linear calibration ranges must be determined whenever there is a significant change in instrument response and every six months for those analytes that periodically approach their linear limit.

12.4.1 For work following the Army Corp of Engineers Shell document, the linear range cannot exceed the level of the high calibration standard on that run. All elements to be reported that exceed the high standard must be reanalyzed on dilution and the results reported from the dilution.

12.5 Initial Calibration Verification (ICV) and Initial Calibration Blank (ICB). After every new calibration, an ICV must be analyzed. The analysis of the ICV may be followed by the analysis of the ICB, although this is not required by the method.

12.5.1 For the ICV, all elements to be reported must be within 10 percent of the true value and the replicates that exceed 5 times the reporting limit must have a relative standard deviation of less than 5 percent. The ICV must be from a different source than the calibration standards and must be near the mid-point of the calibration curve. If the ICV does not meet criteria, then the problem must be identified and corrected before samples can be run and reported for the element(s) that are outside of criteria. Correction of the problem can be verified by rerunning the check standard and showing that it meets QC criteria.

12.5.2 If an ICB is analyzed, than all elements to be reported must be less than the RL (LLOQ). If the ICB is outside of criteria, then the problem must be identified and corrected before samples can be run and reported for the element(s) that are outside of criteria. Correction of the problem can be verified by rerunning the check standard and showing that it meets QC criteria. Analysis of a CCB before running any reportable samples can be used to verify that the system meets calibration blank requirements.

12.6 Continuing Calibration Verification (CCV) and Continuing Calibration Blank (CCB). Analyze the continuing calibration verification solution and the continuing calibration blank after every tenth sample and at the end of the sample run.

12.6.1 For the CCV, all elements to be reported must be within 10 percent of the true value and the replicates that are greater than 5 times the reporting limit must have a relative standard deviation of less than 5 percent. The CCV must be made from the same source as the calibration standards at a concentration near the mid-level of the calibration curve. If an element does not meet the recovery criteria of the CCV (90 to 110%), than no samples can be reported for that element in the area bracketed by the CCV.

12.6.1.1 If the replicate rsd is high, but all replicates are within the recovery limits, then the results can be accepted at the discretion of the reviewer.

12.6.2 For the CCB, all elements to be reported must be less than the reporting limit (LLOQ). If an element does not meet this criteria, then no samples can be reported for that element in the area bracketed by the CCB.

12.7 Interference Check Standard. An interference check standard must be analyzed at the beginning of each analytical run. For all spiked elements, the analyzed results must be within 20 percent of the true values. For unspiked elements, the interfering element solutions must contain less than the absolute value of two times the reporting limit for each element. If this criteria is not met, then no samples containing the elements in question can be reported in the area bracketed by this QC unless the samples contain no significant interferents. This method does not require the analysis of an interfering element check solution at the end of the run. However, this may be required due to meet other method and/or client requirements. Run the ICSA and ICSAB as instructed by the metals lab supervisor or manager or as noted in the program code requirements.

12.8 Low Level Calibration Verification (CRI, CRIB, CRID, CRIA or LLCCV). These are the low level calibration verification standards containing the elements of interest at (or below) the reporting level for each element. A low level check standard at or below the RL/LOQ must be analyzed at the beginning and end of each calibration (analysis) batch. The acceptance criterion for these checks is 70 to 130% recovery for non-DOD work. For DOD, the acceptance criterion for this is 80 to 120%. If an element does not meet this criterion, then all bracketed samples for that element in the concentration range between the low level calibration verification check and the CCV must be reanalyzed. Samples containing concentrations higher than the CCV may be reported as long as CCV criteria are met. The CRI, CRIB, CRID and CRIA nomenclature is used to address different reporting limits for different methods. CRIB is normally used for the DOD LOQ check.

12.8.1 More frequent LCCV checks may be analyzed during the course of the run if system stability at the low end of the calibration is questionable or if the lab wants to ensure that fewer samples will have to be submitted for reanalysis if there is a failed low check at the end of a run.

12.8.2 It is recommended that the CRI check be run bracketing every 4 to 8 hour period of analysis. It may be run as frequently as every 10 samples if the supervisory staff deems that this is necessary.

12.9 Method Blank. The laboratory must digest and analyze a method blank with each set of samples. A minimum of one method blank is required for every 20 sample batch. If the method blank does not contain target analytes at a level that interferes with the project-specific DQOs, then the method blank is considered acceptable.

12.9.1 The default SOP limit for the method blank is that is must be less than one half of the reporting limit.

12.9.2 In addition, the blank is considered acceptable if it is less than 10% of the regulatory limit, or less than 10% of the lowest sample concentration for each analyte in a given preparation batch, whichever is greater.

12.9.3 If the method blank does not meet criteria, then it can be reanalyzed along with any associated samples. If it is still unacceptable, then all associated samples must be redigested and reanalyzed along with the other appropriate batch QC samples

12.10 Lab Control Sample or Spike Blank. The laboratory must digest and analyze a laboratory control sample or spike blank with each set of samples. A minimum of one lab control sample or spike blank is required for every 20 sample batch. The laboratory must assess laboratory performance of the lab control and spike blank against recovery limits of 80 to 120 percent. In house lab control and spike blank limits may also be generated to support these default limits. If the lab control or spike blank is outside of the control limits for a given element, all samples must be redigested and reanalyzed for that element.

12.10.1 If solid lab controls are used, then the manufacturer's limits must be applied.

12.11 Matrix Spike. The laboratory must add a known amount of each analyte to a minimum of 1 in 20 samples. The matrix spike recovery is calculated as shown below. Recoveries must be assessed against default limits of 75 to 125 percent. In house limits may be generated for this method for informational purposes only. If a matrix spike is out of control, then the results must be flagged with the appropriate footnote and it is recommended that a post-digest spike be analyzed for the out of control element(s). If the matrix spike amount is less than one fourth of the sample amount, then the sample cannot be assessed against the control limits and must be footnoted to that effect. Note: Both the matrix spike amount and the sample amount are calculated to the IDL for any given element. Any value less than the IDL is treated as zero.

((Spiked Sample Result - Sample Result) / Amount Spiked) x 100 = matrix spike recovery

12.11.1 If a post-digest spike is required, the sample must be spiked with approximately 2 times the sample level or two times the reporting limits, whichever is greater. Limits of 80 to 120 percent are applied. The serial dilution is used to confirm any matrix effects. The post-digest spike recovery must be footnoted on the matrix spike recovery or otherwise noted in the quality control summary report. If the post-spike recoveries are out of the range of 80 to 120%, then the matrix spike results must be footnoted with a comment that the post-digest spike recovery indicates possible matrix interference.

12.12 Matrix Spike Duplicate (MSD) or Matrix duplicate (DUP). The laboratory must digest a matrix spike duplicate or matrix duplicate sample for a minimum of 1 in 20 samples. The relative percent difference (rpd) between the MSD and the MS or between the DUP and the sample must be assessed. The rpd is calculated as shown below. The control limit for the duplicate rpd is method defined as 20%. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of $\pm$ the reporting limit, then the duplicate is considered to be in control. Note: Both the duplicate amount and the sample amount are calculated to the IDL for any given element. Any value less than the IDL is treated as zero.

12.12.1 If a MSD or duplicate is out of control, then the data must be checked carefully to confirm that the high rpd for a given element is not a result of an analytical problem. If an analytical problem is suspected, the MSD or duplicate must be reanalyzed for confirmation. If the initial and reanalysis are in agreement (within 20%), then the high rpd is a result of preparation or sample issues and further analysis of the initial preparation is not required. If the initial and reanalysis are not in agreement due to an analytical problem, then any affected samples in the associated batch must also be reanalyzed for that element.

12.12.2 If more than 50% of the elements in a sample (that have levels of at least 5 times the reporting limit) have a high RPD, then the MSD or duplicate must be redigested for confirmation, unless the sample matrix is such that the non-homogeneity of the sample is visually apparent. If the results confirm, the results from the original MSD or duplicate must be flagged as indicative of possible sample non-homogeneity. If the results do not confirm, then the whole batch must be digested and reanalyzed.

12.12.3 If 50% or less of the elements in a sample (that have levels of at least 5 times the reporting limit) have a high rpd, then the high rpd(s) must be footnoted as indicating possible sample non-homogeneity unless other problems are suspected. If problems are suspected, the reviewer will initiate redigestion and reanalysis of the batch.

12.12.4 The calculations used to calculate RPD are shown below.

$$\frac{(|\text{MS Result} - \text{MSD Result}|) \times 100}{(\text{MS Result} + \text{MSD Result})/2} = \text{MSD RPD}$$

$$\frac{(|\text{Sample Result} - \text{Duplicate Result}|) \times 100}{(\text{Sample Result} + \text{Duplicate Result})/2} = \text{Duplicate RPD}$$

12.13 Serial Dilution. A serial dilution is required on a frequency of one in 20 samples. For one sample per preparation batch, or whenever matrix interferences are suspected for a batch of samples, a serial dilution must be prepared. Normally the sample used for the serial dilution is the sample that is used for the matrix spike and matrix spike duplicate. For the serial dilution, a 1:5 dilution must be made on the sample. The results of the 1:5 dilution must agree within 10 percent of the true value as long as the sample is greater than 50 times the reporting limit for that element before dilution (or 10 times the reporting limit after dilution) and the sample results are within the linear range. If not, an interference effect must be suspected and the serial dilution result for the element with the suspected interference must be footnoted. The serial dilution is calculated as shown below.

$$\frac{100 \times ((\text{Sample result} - \text{Serial dilution result}))}{\text{Sample result}} = \text{Serial dilution percent difference}$$

12.14 Post Digestion Spike Addition. Post-digest spikes may also be used to determine potential interferences. Check with the metals supervisor for further information on when a post-digest spike must be performed. Recovery limits of 80 to 120 percent must be used to assess post-digest spikes.

12.15 IEC Correction Factor Generation. All interfering element correction factors (IEC's), must be verified and updated a minimum of once every 6 months or whenever instrument conditions change significantly.

12.16 Lower Limit of Quantitation check sample (LLQC). The LLQC is a sample at the reporting limit that is taken through the entire preparation and analytical process. This standard must be analyzed when reporting limits are initial established and on an as needed basis after that. The LLQC is equivalent to the LOQ (Limit of quantitation) standard which must be analyzed quarterly for the DOD QSM 4.1 program. The limits of quantitation are verified when all analytes in the LLQC sample are detected within 30% of their true value. If the limits cannot be verified at the spiked level, then the quantitation limit must be adjusted to a level where verification is successful.

12.17 Calibration Curve. The calibration curve must be prepared daily using a minimum of a calibration blank and one non-zero. The calibration must be verified with LLCCV/CRI and an ICV before any samples can be analyzed. If the curve is not verified as described in section 12.5 or 12.8, then no results can be reported for those elements which did not meet quality control criteria.

13.0 CALCULATIONS

13.1 For water samples, the following calculations must be used. Refer to the QC section for the calculations to be used for the QC samples.

$$\text{original sample concentration of metal } (\mu g/l) = \frac{(\text{conc. in the digestate } (\mu g/l)) \times (\text{final digestate volume (ml)})}{(\text{Initial sample volume (ml)})}$$

13.2 For soil samples, the following calculations must be used.

$$\text{concentration of the metal in the dry sample (mg/kg)} = \frac{(\text{conc. in the digestate (mg/l)} \times \text{final digestate volume(L)})}{(\text{sample wt. (kg)}) \times (\% \text{ solids}/100)}$$

14.0 DOCUMENTATION REQUIREMENTS

14.1 If any samples or QC checks require reanalysis, a brief explanation of the reason must be documented in the raw data. All instrument data must be exported to the LIMS system and a copy of the run log must be included in the logbook by the instrument.

14.2 The Standard Preparation Logbook must be completed for all standard preparations. All information requested must be completed. The Accutest Lot Number must be cross-referenced on the standard vial.

14.3 The Instrument Maintenance Logbook must be completed when any type of maintenance is performed on the instrument. A copy of any outside maintenance reports must also be kept in the log. In addition to the maintenance, the maintenance log must also contain daily information on such items as the profile intensity. Each instrument has a separate log.

14.4 Any corrections to laboratory data must be done using a single line through the error and a reason for the correction. The initials of the person and date of correction must appear next to the correction.

14.5 Supervisory (or peer) personnel must routinely review (at least once per month) all laboratory logbooks to ensure that information is being recorded properly. Additionally, the maintenance of the logbooks and the accuracy of the recorded information must also be verified during this review.

15.0 INSTRUMENT MAINTENANCE

15.1 Recommended periodic maintenance includes the items outlined below.

15.1.1 Change the pump tubing weekly or as needed.

15.1.2 Clean the filter on the recirculating pump approximately once a month and dust off the power supply vents every one to two weeks.

15.1.3 Clean the radial view quartz surface weekly or more often if needed.

15.1.4 Clean the nebulizer, torch, and injector tube every two to four weeks or more often as needed.

15.1.5 Change the sampler tip as needed (every one to two months).

15.1.6 Clean the recirculating pump lines every 3 months or more often if needed.

15.1.7 Clean the slides on the autosampler with methanol and wipe them with a KimWipe saturated with Teflon spray a minimum of once per day.

16.0 POLLUTION PREVENTION & WASTE MANAGEMENT

16.1 Users of this method must perform all procedural steps in a manner that controls the creation and/or escape of wastes or hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids or solids to the environment must be followed. All method users must be familiar with the waste management practices described in section 16.2.

16.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the waste management SOP, EHS004. This document describes the proper disposal of all waste materials generated during the testing of samples as follows:

16.2.1 Non hazardous aqueous wastes.

16.2.2 Hazardous aqueous wastes

16.2.3 Chlorinated organic solvents

16.2.4 Non-chlorinated organic solvents

16.2.5 Hazardous solid wastes

16.2.6 Non-hazardous solid wastes

17.0 ADDITIONAL REFERENCES

17.1 Refer to other SOP's for ICP analysis (CLP, and EPA 200.7 for both DW and WW).

TABLE 1: NORMAL REPORTING LIMITS BY ELEMENT			
Analyte	**Water & Wipe Reporting Limit (µg/l)**	**Soil Reporting Limit (mg/kg)**	**TCLP Reporting Limit (mg/l)**
Aluminum	200	50	
Antimony	6	2	
Arsenic	3	2	0.50
Barium	200	20	1.0
Beryllium	1	0.2	
Cadmium	3	0.5	0.005
Calcium	5000	500	
Chromium	10	1	0.010
Cobalt	50	5	
Copper	10	2.5	
Iron	100	50	
Lead	3	2	0.50
Magnesium	5000	500	
Manganese	15	1.5	
Nickel	10	4.0	
Potassium	10000	1000	
Selenium	10	2	0.50
Silver	10	0.5	0.010
Sodium	10000	1000	
Thallium	2	1	
Vanadium	50	5	
Zinc	20	2	
Boron	100	10	
Molybdenum	20	1	
Palladium	50	5.0	
Sulfur	50	NA	
Silicon	200	20	
Strontium	10	1	
Tin	10	5	
Titanium	10	1	
Tungsten	50	5	
Zirconium	10	2	

TABLE 2: ANALYTICAL LINES ON THE SSTRACE1 AND SSTRACE2	
Element	**Wavelength**
Al	396.1
As	189.0
Ca	317.9
Fe	259.9
Mg	279.0
Mn	257.610
Pb	220.3
Se	196.0
Tl	190.8
V	292.4
Ag	328.0
Ba	455.4
Be	313.0
Cd	228.8
Co	228.6
Cr	267.7
Cu	324.7
K	766.4
Na	589.5
Ni	231.6
Sb	206.8
Zn	206.2
B	208.9
Mo	202.0
Pd	340.4
S	182.0
Sr	407.7
Sn	189.9
Ti	334.9
Si	212.4
W	207.9
Zr	339.1

TABLE 3: CALIBRATION STANDARD LEVELS in ug/l		
Element	**STD A (Blank)**	**STD B**
Ba	0	4000
Be	0	4000
Cd	0	4000
Cr	0	4000
As	0	4000
Se	0	4000
Pb	0	4000
Tl	0	4000
Mn	0	4000
Co	0	4000
Zn	0	4000
Cu	0	4000
Ni	0	4000
Sb	0	4000
Mo	0	4000
B	0	4000
Sn	0	4000
Ti	0	4000
Ag	0	500
V	0	4000
Sr	0	4000
Si	0	10000
Pd	0	4000
W	0	4000
Zr	0	4000
S	0	4000
Al	0	80000
Ca	0	80000
Fe	0	80000
Mg	0	80000
K	0	80000
Na	0	80000

TABLE 4: ICV, and CCV LEVELS		
Element	**ICV Suggested Level in ug/l**	**CCV Suggested Level in ug/l**
Al	40000	40000
As	2000	2000
Ca	40000	40000
Fe	40000	40000
Mg	40000	40000
Mn	2000	2000
Pb	2000	2000
Se	2000	2000
Tl	2000	2000
V	2000	2000
Ag	250	250
Ba	2000	2000
Be	2000	2000
Cd	2000	2000
Co	2000	2000
Cr	2000	2000
Cu	2000	2000
K	40000	40000
Na	40000	40000
Ni	2000	2000
Sb	2000	2000
Zn	2000	2000
B	2000	2000
Mo	2000	2000
Pd	2000	2000
Sr	2000	2000
Sn	2000	2000
Ti	2000	2000
Si	5000	5000
W	2000	2000
Zr	2000	2000
S	2000	2000

TABLE 5: SUGGESTED CONCENTRATIONS OF METALS IN THE MATRIX SPIKE AND SPIKE BLANK			
Element	**Soils Final Concentration in mg/kg**	**Aqueous Final Concentration in μg/l**	**TCLP Leachates Final Concentration in mg/l**
Ag	10	50	0.05
Al	5400	2000	
As	400	2000	2.0
B	100	2000	
Ba	400	2000	10.0
Be	10	50	
Ca	1250	25000	
Cd	10	50	0.05
Co	100	500	
Cr	40	200	0.20
Cu	50	250	
Fe	5200	1000	
K	1250	25000	
Mg	1250	25000	
Mn	100	500	
Mo	100	2000	
Na	1250	25000	
Ni	100	500	
Pb	100	500	2.0
Sb	100	500	
Se	400	2000	2.0
Tl	400	2000	
V	100	500	
Zn	100	500	
S	100	2000	
Sn	100	2000	
Sr	100	2000	
Ti	100	2000	
Si	200	4000	
Pd	100	2000	
W	100	2000	
Zr	100	2000	

TABLE 8: SUGGESTED CONCENTRATIONS OF METALS IN THE QUALITY CONTROL SAMPLE LOW CHECK (CRI or CRIB) SOLUTION	
Element	**Final Concentration in µg/l**
Sb	6
As	8
Ba	200
Be	2
Cd	3
Cr	10
Co	50
Cu	10
Pb	3
Mn	15
Ni	10
Se	10
Tl	10
V	50
Zn	20
B	100
Bi	20
Li	20
Mo	20
Pd	50
Sr	10
S	50
Sn	10
Ti	10
W	50
Zr	10
Ag	5
Si	200
Al	200
Ca	5000
Fe	100
Mg	5000
K	5000
Na	5000

TABLE 9: SUGGESTED CONCENTRATIONS OF METALS IN THE QUALITY CONTROL SAMPLE LOW CHECK (CRID) SOLUTION	
Element	**Final Concentration in µg/l**
Sb	3
As	3
Ba	4
Be	1
Cd	1
Cr	2
Co	3
Cu	2
Pb	2.5
Mn	3
Ni	4
Se	5
Tl	2
V	2
Zn	10
B	10
Bi	
Li	
Mo	
Pd	
Sr	
S	
Sn	
Ti	
W	
Zr	
Ag	1
Si	
Al	100
Ca	1
Fe	
Mg	100
K	2000
Na	1000

TABLE 10: SUGGESTED CONCENTRATIONS OF METALS IN THE QUALITY CONTROL SAMPLE LOW CHECK (CRIA) SOLUTION	
Element	**Final Concentration in µg/l**
Sb	20
As	20
Ba	
Be	
Cd	
Cr	
Co	
Cu	
Pb	20
Mn	
Ni	
Se	20
Tl	
V	
Zn	
B	
Bi	
Li	
Mo	
Pd	
Sr	
S	
Sn	
Ti	
W	
Zr	
Ag	
Si	
Al	500
Ca	
Fe	500
Mg	
K	
Na	

Lab Manager

QA Manager

Effective Date: 6/11/13

TEST NAME: METHOD 8270D, SEMIVOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS)

REFERENCE: SW846 8270D (Revision 4, February 2007)

Revised Sections: ***10.3.2.4.1, 10.3.2.4.2***

SCOPE AND APPLICATION

1.1 The following method describes the analytical procedure that is utilized by Accutest to analyze semivolatile organic compounds in extracts prepared from all types of solid waste matrices, soils, and water samples. Options are incorporated for the analysis of sixteen (16) polyaromatic hydrocarbons (PAH) and other compounds listed in table 8A by selected ion monitoring GC/MS (GC/MS-SIM).

1.2 Table 1 lists the neutral, acidic, and basic organic compounds that can be determined by this method. The applicable concentration range of this method is compound and instrument dependent. Some compounds may require special treatment due to the limitations caused by sample preparation and/or chromatographic problems.

2.0 SUMMARY OF METHOD

2.1 This method is performed in accordance with the following extraction methodologies in SW846: 3510, 3520, 3545, 3550 and 3580.

2.2 The resultant methylene chloride extract is injected into a tuned and calibrated GC/MS system equipped with a fused silica capillary column. The GC column is temperature-programmed to separate the analytes, which are then detected with a mass spectrometer (MS) connected to the gas chromatograph.

2.3 The peaks detected are qualitated by comparison to characteristic ions and retention times specific to the known target list of compounds.

2.4 Once identified, the compound is quantitated by internal standard techniques with an average response factor generated from the calibration curve.

2.5 Additional unknown peaks with a response greater than 10 % of the closest internal standard may be processed through a library search with comparison to a NIST98 database. An estimated concentration is quantitated by assuming a response factor of 1.

2.6 This method includes analytical options for PAHs and other selected compounds by GC/MS-SIM. The extract is fortified with an additional SIM specific internal standard mix and analyzed using selected ions that are characteristic of the compounds of interest following the analysis of lower concentration calibration standards analyzed under the same MS scan conditions. Qualitative and quantitative identification is conducted using the procedures employed for full scan analysis.

3.0 REPORTING LIMIT & METHOD DETECTION LIMIT

3.1 Reporting Limit. The reporting limit for this method is established at either method detection limit or the lowest concentration standard in the calibration curve, depending on the requirements of different regulatory programs. Detected concentrations below this concentration cannot be reported without qualification. See table 9.

3.1.1 Compounds detected at concentrations between the reporting limit and MDL are quantitated and qualified as "J", estimated value. Program or project specifications may dictate that "J" qualified compounds are not to be reported.

3.2 Method Detection Limit. Experimentally determine MDLs using the procedure specified in 40 CFR, Part 136, Appendix B. This value represents the lowest reportable concentration of an individual compound that meets the method qualitative identification criteria.

3.2.1 Experimental MDLs must be determined annually for this method.

3.2.2 Process all raw data for the replicate analysis in each MDL study. Forward the processed data to the QA group for archiving.

4.0 DEFINITIONS

BATCH - a group of samples which behave similarly with respect to the sampling or the testing procedures being employed and which are processed as a unit. For QC purposes, if the number of samples in a group is greater than 20, then each group of 20 samples or less will all be handled as a separate batch.

BLANK - an analytical sample designed to assess specific sources of laboratory contamination.

CONTINUING CALIBRATION - a mid-range calibration check standard run every 12 hours to verify the initial calibration of the system.

EXTRACTED ION CURRENT PROFILE (EICP) - a plot of ion abundance versus time (or scan number) for ion(s) of specified mass (Es).

INITIAL CALIBRATION - analysis of analytical standards for a series of different specified concentrations which cover the working range of the instrument; used to define the linearity and dynamic range of the response of the mass spectrometer to the target compounds.

INTERNAL STANDARDS - compounds added to every standard, blank, matrix spike, matrix spike duplicate, and sample extract at a known concentration, prior to analysis. Internal standards are used as the basis for quantitation of the target compounds and must be analytes that are not sample components.

MATRIX - the predominant material of which the sample to be analyzed is composed.

MATRIX SPIKE - aliquot of a matrix (water or soil) fortified (spiked) with known quantities of specific compounds and subjected to the entire analytical procedure in order to indicate the appropriateness of the method for the matrix by measuring recovery.

MATRIX SPIKE DUPLICATE - a second aliquot of the same matrix as the matrix spike (above) that is spiked in order to determine the precision of the method.

METHOD BLANK - an analytical control consisting of all reagents, internal standards and surrogate standards, is carried throughout the entire preparatory and analytical procedure. The method blank is used to define the level of laboratory, background and reagent contamination.

METHOD DETECTION LIMITS (MDLs) - The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte. MDLs must be determined approximately once per year for frequently analyzed parameters.

PERCENT DIFFERENCE (%D) - As used to compare two values, the percent difference indicates both the direction and the magnitude of the comparison, i.e., the percent difference may be either negative, positive, or zero. (In contrast, see relative percent difference.)

PRIMARY QUANTITATION ION - a contract specified ion used to quantitate a target analyte.

REAGENT WATER - water in which no interferant is observed at or above the minimum detection limit of the parameters of interest.

RECONSTRUCTED ION CHROMATOGRAM (RIC) - a mass spectral graphical representation of the separation achieved by a gas chromatograph; a plot of total ion current versus retention time.

RELATIVE PERCENT DIFFERENCE (RPD) - As used to compare two values, the relative percent difference is based on the mean of the two values, and is reported as an absolute value, i.e., always expressed as a positive number or zero. (In contrast, see percent difference.)

RELATIVE RESPONSE FACTOR (RRF) - a measure of the relative mass spectral response of an analyte compared to its internal standard. Relative Response Factors are determined by analysis of standards and are used in the calculation of concentrations of analytes in samples.

RELATIVE RETENTION TIME (RRT) - the ratio of the retention time of a compound to that of a standard (such as an internal standard).

RESOLUTION - also termed separation or percent resolution, the separation between peaks on a chromatogram, calculated by dividing the depth of the valley between the peaks by the peak height of the smaller peak being resolved, multiplied by 100.

INITIAL CALIBRATUION VERIFICATION (SECOND SOURCE CALIBRATION STANDARD) - a standard from a separate source than the calibration curve that is used to verify the accuracy of the calibration standards. An external check must be run whenever an initial calibration is performed.

SURROGATES - pure analytes added to every blank, sample, matrix spike, matrix spike duplicate, and standard in known amounts before extraction or other processing; used to evaluate analytical efficiency by measuring recovery. Surrogates are brominated, fluorinated, or isotopically labeled compounds not expected to be detected in environmental media.

5.0 HEALTH & SAFETY

5.1 The analyst must follow normal safety procedures as outlined in the Accutest Health and Safety Plan and Personal Protection Policy, which include the use of safety glasses and lab coats. In addition, all acids are corrosive and must be handled with care. Flush spills with plenty of water. If acids contact any part of the body, flush with water and contact the supervisor.

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical must be treated as a potential health hazard. Exposure to these reagents must be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets is made available to all personnel involved in these analyses.

5.3 The following analytes covered by this method have been tentatively classified as known or suspected human or mammalian carcinogens: benzo(a)anthracene, benzidine, 3,3'-dichlorobenzidine, benzo(a)pyrene, dibenzo(a,h)anthracene, N-nitrosodimethylamine, and 4,4'-DDT. Prepare primary standards of these toxic compounds in a hood. A NIOSH/Mass approved toxic gas respirator must be worn when the analyst handles high concentrations of these toxic compounds.

6.0 INTERFERENCES

6.1 The data from all blanks, samples, and spikes must be evaluated for interferences.

6.2 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other stages of sample processing. Refer to "The Preparation of Glassware for Extraction of organic contaminants" SOP for practices utilized in the extraction department.

6.3 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the industrial complex or municipality being sampled.

6.4 To reduce carryover when high-concentration samples are sequentially analyzed, the syringe must be rinsed out between samples with solvent. Whenever an unusually concentrated sample is encountered, it must be followed by the analysis of solvent to check for cross contamination.

7.0 SAMPLE COLLECTION, PRESERVATION, & HOLDING TIMES

7.1 Water samples may be collected in 1-liter glass bottles with Teflon insert in caps. Soil samples may be collected in 250-ml wide-mouth amber glass bottles.

7.1.1 Samples must be taken with care so as to prevent any portion of the collected sample coming in contact with the sampler's gloves, thus avoiding possible phthalate contamination.

7.2 Test all aqueous samples for residual chlorine using test paper for free and total chlorine. If the sample tests positive for residual chlorine, add 80 mg of sodium thiosulfate to each liter of sample.

7.3 The samples must be protected from light and refrigerated at $\leq$ 6° C from the time of receipt until extraction and analysis.

7.4 Store the sample extracts at -10 °C in amber vials (protected from light), in sealed vials equipped with unpierced PTFE-lined septa.

7.5 HOLDING TIME

7.5.1 Aqueous samples must be extracted within 7 days of sampling.

7.5.2 Soil, sediments and concentrated waste samples must be extracted within 14 days of sampling.

7.5.3 Extracts must be analyzed within 40 days following extraction.

8.0 APPARATUS & MATERIALS

8.1 GAS CHROMATOGRAPH/MASS SPECTROMETER SYSTEM

8.1.1 Gas Chromatograph. HP-5890, HP-6890, or Agilent 6890-N which includes an analytical system that is complete with a temperature programmable gas chromatograph and all required accessories including syringes, capillary chromatographic columns, and gases.

8.1.1.1 The injection port is designed for split or splitless injection with capillary columns.

8.1.1.2 The capillary column is directly coupled to the source.

8.1.2 Column.

8.1.2.1 30 m x 0.25 mm fused silica (0.25 μm film thickness) DB-5MS or equivalent capillary column. Condition the column as per manufacture's directions.

8.1.3 Mass Spectrometer (HP-5972, HP-5973 or Agilent 5975).

8.1.3.1 Full Scan Mode -Capable of scanning from 35-500 amu every 1 second or less utilizing 70 volt (nominal) electron energy in the electron impact ionization mode.

8.1.3.2 SIM Mode- Capable of selective ion grouping at specified retention times for increased compound sensitivity (table 2a).

8.1.3.3 Capable of producing a mass spectrum which meets all the EPA performance criteria in Table 3 when injecting 50 ng of Decafluorotriphenyl phosphine (DFTPP).

8.2 DATA SYSTEM

8.2.1 Acquisition and Instrument Control: HP Chemstation. A computer system is interfaced to the mass spectrometer that allows the continuous acquisition and storage on machine readable media (disc) of all mass spectra obtained throughout the duration of the chromatographic program.

8.2.2 Data Processing: HP Enviroquant. The software accommodates searching of GC/MS data files for analytes which display specific fragmentation patterns. The software also allows integrating the abundance of an EICP between specified time or scan number limits. The

data system includes the NIST98 spectra library for qualitative searches of non-target compounds present in the chromatogram. It flags all data files that have been edited manually by laboratory personnel.

8.2.3 Offline Magnetic Tape Storage Device (Lagato Networker) - the magnetic tape storage device copies data for long term, offline storage.

8.3 SYRINGE

8.3.1 10 μl graduated, auto sampler (Hamilton or equiv.).

8.3.2 Micro liter syringes, various sizes

9.0 REAGENTS AND STANDARDS

9.1 Solvents - Ultra pure, chromatography grade methylene chloride and acetone.

9.2 Stock Standard Solutions.

9.2.1 Certified, commercially prepared standards, from two separate sources are used.

9.2.1.1 Base Neutrals.

- Base/Neutrals Mix #1 (Absolute: Semivolatile Organics Standard Mix # 1).
- Base/Neutrals Mix #2 (Absolute: Semivolatile Organics Standard Mix # 2).
- PAH Mix (Absolute: Semivolatile Organics Standard Mix # 7).
- PAH Mixture #2 (Ultra).
- PAH Selected Ion Monitoring Mixture
- Benzidines Mix (Absolute: Semivolatile Organics Standard Mix # 6).
- Toxic Substances #2 (Absolute: Semivolatile Organics Standard Mix # 5).
- Pyridines Mixture (Ultra).
- Additonal requested compound(s) mix (Absolute).
- Base Neutral Mixture (2nd Source).

Acids.

- Phenols Mix (Absolute: Semivolatile Organics Standard Mix # 8).
- Toxic Substances #1(Absolute: Semivolatile Organics Standard Mix # 4).
- Acid Mixture (2nd Source).Internal Standard Mixtures.

9.2.2 Internal Standard Mixtures

9.2.2.1 Ultra (or equivalent) at a concentration of 4,000 μg/ml for each of the following compounds.

Full Scan

- 1,4-Dichlorobenzene-d4
- Naphthalene-d8

- Acenaphthene-d10
- Phenanthrene-d10
- Chrysene-d12
- Perylene-d12

SIM

- 1,2-Dichlorobenzene-d4
- 1-Methylnaphthalene-d10
- Fluorene-d10
- Fluoranthene-d10
- Benzo(a)pyrene-d12

9.2.2.2 The internal standards must permit most of the components of interest in a chromatogram to have retention times of 0.8 - 1.20 relative to one of the internal standards.

9.2.2.3 Each 1 ml sample extract, and standard undergoing analysis must be spiked with 10 μl of the internal standard mixtures, resulting in a concentration of 40 μg/ml of each internal standard for full scan analysis and 4 ug/ml for SIM analysis.

9.2.3 Surrogate Standard Mixture.

9.2.3.1 B/N Surrogate Standard Mix: RESTEK (or equivalent) at a concentration of 5,000 μg/ml each surrogate compound.

- Nitrobenzene-d5.
- 2-Fluorobiphenyl.
- p-Terphenyl-d14.

9.2.3.2 Acid Surrogate Standard Mix: RESTEK (or equivalent) at a concentration of 7,500 μg/ml each surrogate compound.

- Phenol-d5.
- 2-Fluorophenol.
- 2,4,6-Tribromophenol.

9.2.4 DFTPP Tune Stock.

9.2.4.1 Protocol (or equivalent) at a concentration of 2,500 μg/ml for the following compounds.

- Decafluorotriphenylphosphine.
- 4,4'-DDT.
- Benzidine.
- Pentachlorophenol.

9.2.5 Store at -10 ^{o}C or less when not in use or according to the manufacturer's documented holding time and storage temperature recommendations. Stock standard solutions must be replaced after 1 year or sooner if manufacture's expiration date comes first or comparison with quality control check samples indicates degradation.

9.3 Surrogate Spiking Solutions.

9.3.1 Two surrogate spiking solutions, base/neutral surrogate solution and acid surrogate solution, at a concentration of 100 μg/ml are prepared in Extraction. Spike each sample, and blank with 0.5 ml of each solution, prior to extraction, for a final concentration of 50 μg/l of each surrogate compound in the extract.

9.3.2 A calibration range must be constructed for the surrogate compounds. Accordingly, appropriate amounts of surrogates are mixed with each calibration solution to define a range similar to the target compounds.

9.3.3 Store at -10 °C or less or according to the manufacturer's documented storage temperature recommendations. Prepare fresh surrogate spiking solutions every year, or sooner, if the manufacturer's expiration dates come first or if the solution has degraded or evaporated.

9.4 Intermediate Calibration Standard Solution.

9.4.1 The calibration stock solution is prepared by adding an appropriate amount of each stock and surrogate compounds into a 10 ml volumetric flask. Dilute the solution to the volume with methylene chloride and mix thoroughly. Refer to Table 7A for details.

9.5 Calibration Standards.

9.5.1 Initial Calibration Standards.

9.5.1.1 Calibration standards containing the surrogate compounds must be made by quantitative dilutions of the above intermediate solution. The calibration standards are prepared at a minimum of five concentrations to cover the range of 1 - 100 μg/ml for full scan and 0.02 – 5ug/ml for SIM, depending upon project specific requirements. Suggested levels and preparations are shown in Table 7A and 7B.

9.5.2 Continuing Calibration Verification.

9.5.2.1 The concentration of the mid range standard used for continuing calibration verification is alternated between 25 and 50 μg/ml for full scan and 2.5 and 1.0 for SIM.

9.5.3 Store the calibration standards in a refrigerator at $\leq$ 6 °C and prepare every 6 months or before the manufacturer's expiration date, whichever is sooner. Standards must be replaced immediately if the analysis of check standards indicates degradation.

9.6 Initial Calibration verification (ICV) -Second source calibration check standard.

9.6.1 The ICV standard is prepared per Table 7E, using the intermediate solutions prepared in Extraction.

9.6.2 The ICV is analyzed after each initial calibration.

9.7 Daily GC/MS Performance Checks.

9.7.1 The solution is prepared at 50 μg/ml by making a 1:50 dilution of DFTPP stock solution (Section 9.2.4) in methylene chloride.

9.8 Matrix Spike Solutions.

9.8.1 The matrix spike solutions for both Base/Neutral and Acid are prepared in Acetone at a concentration of 100 μg/ml for each compound. Prepare the matrix spike, matrix spike duplicate and blank spike by spiking the selected sample and the blank with 0.5 ml of these solutions for a final concentration of 50 μg/l of each compound.

9.9 All organic new standard solutions are analyzed prior to use to verify the accuracy of the prepared concentration.

9.9.1 The prepared standard solution is analyzed using the determinative (instrumental) technique for the method.

9.9.2 The solution is analyzed following the completion of instrument calibration or a calibration check.

9.9.3 The concentration of the standard solution is determined using the software routines used in determining the acceptability of calibration verification.

9.9.4 The data is evaluated and the percent difference determined. The standard solution is approved for use if all designated compounds are present in the solution and the percent difference is less than the established criteria (±20%).

10.0 CALIBRATION

10.1 Initial Calibration.

10.1.1 The calibration range covered for routine analysis under RCRA employs standards of 1, 2, 5, 10, 25, 50, 80, 100 μg/ml for full scan and 0.02, 0.05, 0.10, 0.20, 1.0, 2.5, 5.0 ug/ml for SIM. A minimum of five standards must be run sequentially. The reporting limit is established by the concentration of the lowest standard analyzed during the initial calibration. Lower concentration standard may be needed to meet the reporting limit requirements of state specific regulatory program. The linear range covered by this calibration is the highest concentration standard.

10.1.2 A calibration range must be constructed for each surrogate compound. Accordingly, add appropriate amounts of surrogate spiking solutions to the calibration solution to define a range similar to the target compounds.

10.1.3 Aliquot 1 ml of each calibration standard into a 2 ml crimp top vial.

10.1.4 Prior to analysis, add 10 μl of the applicable (Full scan and/or SIM) internal standard solution (Section 9.2.2) to each standard. This results in a concentration of 40 μg/ml (Full scan) and 4ug/ml (SIM) for each internal standard.

10.1.5 Analyze the standard solutions using the conditions established in Section 11.0. Each analyte is quantitatively determined by internal standard technique using the closest eluting internal standard and the corresponding area of the major ion. See Table 6.

10.1.6 The Response Factor (RF) is defined in Section 13.1. Calculate the mean RF for each target analyte, using minimum of five RF values calculated from the initial calibration curve.

10.1.7 For the initial calibration to be valid, the following criteria must be met.

10.1.7.1 The percent relative standard deviation (% RSD) (see Section 13.2) of all target analytes must be less than or equal to 20%.

10.1.7.2 If the %RSD of any individual compound is $\geq$20%, employ an alternative calibration linearity model. Specifically, linear regression using a least squares approach may be employed.

10.1.7.2.1 If a linear regression is employed, select the linear regression calibration option of the mass spectrometer data system. Do not force the regression line through the origin and do not employ 0,0 as a sixth calibration standard.

10.1.7.2.2 The correlation coefficient (r value) must be $\geq$0.99 for each compound to be acceptable.

10.1.7.2.2.1 When calculating the calibration curves using the linear regression model, a minimum quantitation check on the viability of the lowest calibration point must be performed by re-fitting the response from the low concentration calibration standard back into the curve.

10.1.7.2.2.2 The recalculated concentration of the low calibration point must be within $\pm$ 30% of the standard's true concentration.

10.1.7.2.3 If more than 10% of the compounds included with the initial calibration exceed the 20% RSD limit and do not meet the minimum correlation coefficient for the linear calibration option, then the chromatographic system is considered too reactive for the analysis to begin. Perform corrective action and recalibrate if the calibration criteria cannot be achieved.

10.1.7.3 It is recommended that the minimum response factor for the most common target analytes in the following table must be demonstrated for each individual calibration level as a means to ensure that these compounds are behaving as expected.

Minimum Response Factor Table

Semivolatile Compounds	Minimum Response Factor (RF)
Benzaldehyde	0.010
Phenol	0.800

Bis (2-chloroethyl) ether	0.700
2-Chlorophenol	0.800
2-Methylphenol	0.700
2,2'-Oxybis-(1-chloropropane)	0.010
Acetophenone	0.010
4-Methylphenol	0.600
N-Nitroso-di-n-propylamine	0.500
Hexachloroethane	0.300
Nitrobenzene	0.200
Isophorone	0.400
2-Nitrophenol	0.100
2,4-Dimethylphenol	0.200
Bis(2-chloroethoxyl)methane	0.300
2,4-Dichlorophenol	0.200
Naphthalene	0.700
4-Chloroaniline	0.010
Hexachlorobutadiene	0.010
Caprolactam	0.010
4-Chloro-3-methylphenol	0.200
2-Methylnaphthalene	0.400
Hexachlorocyclopentadiene	0.050
2,4,6-Trichlorophenol	0.200
2,4,5-Trichlorophenol	0.200
1,1'-Biphenyl	0.010
2-Chloronaphthalene	0.800
2-Nitroaniline	0.010
Dimethyl phthalate	0.010
2,6-Dinitrotoluene	0.200
Acenaphthylene	0.900
3-Nitroaniline	0.010
Acenaphthene	0.900
2,4-Dinitrophenol	0.010
4-Nitrophenol	0.010
Dibenzofuran	0.800
2,4-Dinitrobenzene	0.200
Diethyl phthalate	0.010
1,2,4,5-Tetrachlorobenzene	0.010
4-Chlorophenyl-phenyl ether	0.400
Fluorene	0.900
4-Nitroaniline	0.010
4,6-Dinitro-2-methylphenol	0.010
4-Bromophenyl-phenyl ether	0.100
N-Nitrosodiphenylamine	0.010
Hexachlorobenzene	0.100
Atrazine	0.010
Pentachlorophenol	0.050
Phenanthrene	0.700
Anthracene	0.700

Carbazole	0.010
Di-n-butyl phthalate	0.010
Fluoranthene	0.600
Pyrene	0.600
Butyl benzyl phthalate	0.010
3,3'-Dichlorobenzidine	0.010
Benzo(a)anthracene	0.800
Chrysene	0.700
Bis-(2-ethylhexyl)phthalate	0.010
Di-n-octyl phthalate	0.010
Benzo(b)fluoranthene	0.700
Benzo(k)fluoranthene	0.700
Benzo(a)pyrene	0.700
Indeno(1,2,3-cd)pyrene	0.500
Dibenz(a,h)anthracene	0.400
Benzo(g,h,i)perylene	0.500
2,3,4,6-Tetrachlorophenol	0.010

10.1.7.3.1 Due to the large number of compounds, some compounds will fail to meet the minimum response factor criteria. They may be used as qualified data or estimated values for screening purposes. Non-detects may be reported if adequate sensitivity has been demonstrated at the applicable lower quantitation limit.

10.1.7.4 The initial calibration criteria for this method applies to all additional compounds of concern specified by the client.

10.1.7.5 The relative retention times of each target analyte in each calibration standard must agree within 0.06 relative retention time units.

10.1.7.6 Structural isomers that produce very similar mass spectra are identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is more than 50% of the average of the two peak heights. Otherwise structural isomers are identified as isomeric pairs. The resolution must be verified on the mid - point concentration of the initial calibration (e.g., benzo(b)flouranthene and benzo(k)fluoranthene). Print the check and keep it on file.

10.2 Initial Calibration Verification (ICV) - Source Calibration Check Standard.

10.2.1 The calibration is verified with a calibration check standard at 50 μg/ml (Full scan) or 1ug/ml (SIM) from an external source (Section 9.6). It must be analyzed immediately following the initial calibration.

10.2.2 The percent difference (% D) (Section 13.3) for this standard must meet the criteria of 30% for all the target compounds.

10.2.2.1 If % D is greater than 30%, reanalyze the second source check. If the criteria cannot be met upon re-injection, re-prepare the second source solution using a fresh ampoule and repeat the process.

10.2.2.2 If the %D criteria cannot be achieved after re-preparation of the second source, prepare a third source and repeat the process. Make fresh calibration standards using one of the two standard sources that match each other.

10.3 Continuing Calibration Verification Standard - CCV

10.3.1 A calibration verification standard at close mid-level concentration of the initial calibration range at alternating 25 and 50ug/ml for full scan and 2.5ug/ml and 1ug/ml for SIM must be acquired every 12 hrs.

10.3.1.1 The calibration verification standard selected must be near concentration of the midpoint calibration standard or near the action level for the project specified.

10.3.2 For the continuing calibration to be valid, all of the following specified criteria must be met.

10.3.2.1 Each of the most common target analytes in the calibration verification standard must meet the minimum response factors as noted in the Minimum Response Factor Table in section 10.1.7.3.

10.3.2.2 All target compounds of interest must be evaluated using a 20% D criteria. If the percent difference or percent drift for a compound is less than or equal to 20%, then the initial calibration for that compound is assumed to be valid.

10.3.2.3 Due to the large numbers of compounds that may be analyzed by this method, it is expected that some compounds will fail to meet the 20% D criterion. If the criterion is not met (i.e., greater than 20% difference or drift) for more than 20% of the compounds included in the initial calibration, then corrective action must be taken prior to the analysis of samples.

10.3.2.4 In cases where compounds fail, they may still be reported as non-detects if it can be demonstrated that there was adequate sensitivity to the compound at the applicable quantitation limits. For situation when the failed compound is present, the concentrations must be reported as estimated.

10.3.2.4.1 Compounds with response factors that exceed the 20% D in the CCV compared to the initial calibration with high bias may only be reported when the target analyte is non-detect.

10.3.2.4.2 Compounds that do not meet the 20% D in the CCV compared to the initial calibration due to low response factors can only be reported if the low sensitivity of the instrument is still achieved. This sensitivity must be verified by running a low level standard check at 2-4 times the MDL. If a positive result for the compound is found then adequate sensitivity has been demonstrated and the run can proceed. Non-detect results for samples may be reported, positive results are re-analyzed. This low level sensitivity check does not apply to the PAH compounds.

10.3.2.5 The resolution check for structural isomers must be verified for each CCV standard Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 50% of the average of the two peak heights. Otherwise structural isomers are identified as isomeric pairs. Print the check and keep it on file.

10.3.3 If the first continuing calibration verification does not meet criteria, a second standard may be injected after notifying the team leader/manager and checking the system for defects.

10.3.3.1 A continuing calibration check is allowed to be repeated only once; if the second trial fails, a new initial calibration must be performed or refer to section 10.3.2.4. In situations where the first check fails to meet the criteria, the instrument logbook must have clear documented notations as to what the problem was and what corrective action was implemented to enable the second check to pass.

10.3.4 If the verification criteria cannot be achieved, a new initial calibration must be performed or refer to section 10.3.2.4.

10.3.5 If any of the internal standard areas change by a factor of two (- 50% to + 100%) or the retention time changes by more than 30 seconds from the midpoint standard of the last initial calibration, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate.

10.3.5.1 Reanalyze the continuing calibration standard. New initial calibration is required if reanalyzed standard continues to fail the internal standard requirements.

10.3.5.2 All samples analyzed while the system was out of control must be reanalyzed following corrective action.

11.0 PROCEDURE

11.1 Instrument Conditions.

11.1.1 Recommended instrument conditions are listed in Table 2 and 2a (SIM only). Modifications of parameters specified with an asterisk are allowed as long as criteria of calibration are met. Any modification must be approved by team leader/manger. DFTPP, Standards, QC and samples must all be run under the exact same operating conditions, including EM voltage.

11.2 Daily GC/MS Performance Checks.

11.2.1 Mass Spectrometer Tuning. Every 12-hour, inject 1 μl of 50 ng/μl DFTPP solution directly on to the column.

11.2.2 The GC/MS system must be checked to verify that acceptable performance criteria are achieved (see Table 3).

11.2.3 This performance test must be passed before any sample extracts, blanks or standards are analyzed. Evaluate the tune spectrum using three mass scans from the chromatographic peak and a subtraction of instrument background.

11.2.3.1 Select the scans at the peak apex and one to each side of the apex.

11.2.3.2 Calculate an average of the mass abundances from the three scans.

11.2.3.3 Background subtraction is required. Select a single scan in the chromatogram that is absent of any interfering compound peak and acquired within no more than 20 scans to the elution of DFTPP. The background subtraction must be designed only to eliminate column bleed or instrument background ions. Do not subtract part of the tuning compound peak.

11.2.4 If all the criteria are not achieved, the analyst must retune the mass spectrometer with team leader/manager and repeat the test until all criteria are met.

11.2.4.1 Alternatively, an additional scan on each side of the peak apex may be selected and included in the averaging of the mass scans. This will provide a mass spectrum of five averaged scans centered on the peak apex. NOTE: The selection of additional mass scans for tuning may only be performed with supervisory approval on a case by case basis.

11.2.5 The injection time of the acceptable tune analysis is considered the start of the 12-hour clock.

11.2.6 In order to assess GC column performance and injection port inertness, the DFTPP tune standard also contains appropriate amount of 4,4'-DDT, benzidine and pentachlorophenol.

11.2.7 All subsequent standards, samples, MS/MSDs, and blanks associated with a DFTPP analysis must use the identical mass spectrometer instrument conditions.

11.2.6.1 Injection Port Inertness Check.

11.2.6.1.1 The injection port inertness of the GC portion of the GC/MS is evaluated by the percent breakdown of 4,4'-DDT. DDT is easily degraded in the injection port. Breakdown occurs when the injection port liner is contaminated by high boiling residue from sample injection or when the injector contains metal fittings. Check for degradation problems by injecting a GC/MS tune standard containing 4,4'-DDT every 12 hour, regardless of whether DDT is a target analyte. The degradation of DDT to DDE and DDD must not exceed 20%, in order to proceed with calibration procedures. Refer to Section 13.7 for calculation. Print the check and keep it on file.

11.2.6.2 Column Performance Check.

11.2.6.2.1 The condition of the GC column is evaluated by the tailing of benzidine and pentachlorophenol every 12 hour. Benzidine and pentachlorophenol must be present at their normal responses, with no visible peak tailing, as demonstrated by the peak tailing factors. The tailing factor criteria for benzidine (base-neutral fraction) must be ≤ 2 and for pentachlorophenol (acid fraction) must be ≤ 2. Print the check daily and keep on file:

11.2.6.3 If degradation is excessive and/or poor chromatography is observed, the injector port may require cleaning. It may also be necessary to break off the first 6-12 in. of the capillary column.

11.3 Initial Calibration

11.3.1 Refer to Section 10.1.

11.4 Initial calibration Verification (ICV) - Second Source Calibration Check

11.4.1 This standard must at least be analyzed when initial calibration provided. Refer to Section 10.2.

11.5 Continuing Calibration Checks

11.5.1 Refer to Section 10.3.

11.6 Sample Analysis.

11.6.1 Allow the sample extract to warm to room temperature. Spike 10 μl of the appropriate internal standard mix (4,000 μg/ml for full scan and 400ug/ml for SIM) into 1 ml sample extract, just prior to analysis. This is equivalent to a concentration of 40 μg/ml (full scan) and 4ug/ml (SIM) of each internal standard.

11.6.2 Inject 1 μl aliquot of the sample extract into the GC/MS system. A splitless injection technology is used.

11.6.3 If the response for any ion of interest exceeds the working range of the GC/MS system, dilute a stored extract if available and reanalyze.

11.6.4 When the extracts are not being used for the analyses, store them at -10^{o}C, protected from light, in sealed vials equipped with unpierced PTFE-lined septa.

11.7 Sample Dilution

11.7.1 Establish dilution of sample in order to fall within calibration range or to minimize the matrix interference.

- Utilize screen data (specific project only).
- Utilize acquired sample data.
- Utilize the history program or approval from client/project.
- Sample characteristics (appearance, odor).

11.7.2 If no lower dilution has been reported, the dilution factor chosen must keep the response of the largest peak for a target analyte in the upper half of the initial calibration range of the instrument.

11.7.3 Preparing Dilutions.

11.7.3.1 Prepare sample dilutions quantitatively. Dilute the sample extract with methylene chloride using logical volume to volume ratios, i.e., 1:5, 1:10, 1:50, etc. Large dilutions may require serial dilutions or the use of a Class A 10 ml volumetric flask.

11.7.3.2 Syringe dilutions. – Calibrated syringes are used to prepare dilutions. Add the appropriate amount of methylene chloride to a clean autosampler vial. Add the proper amount of sample using a calibrated syringe of the appropriate volume for the dilution. Add sufficient internal standard to maintain a concentration of 40ug/ml. Cap the vial and gently shake to disperse the sample through the solvent.

11.7.3.3 Volumetric Flask Dilutions – Large dilutions may require the use of a 10 ml Class A Volumetric flask.

11.8 Establishing Search Criteria for target compounds. Search criteria for each compound listed in the method must be entered into the method quantitation/identification file in the Enviroquant software package. This activity must be performed before attempting qualitative and quantitative analysis on any acquired data file. The search criteria are based on compound retention time and the characteristic ions from the reference mass spectrum. Characteristic ions are defined as the three ions of greatest relative intensity, or any ions over 30% relative intensity, if less than three such ions occur in the reference spectrum. The number of secondary ions displayed for each compound search varies between compounds.

11.8.1 Select the primary ion for the target compound from the characteristic ions in Table 6. If multiple characteristic ions are listed, the first ion is the major (primary) ion. Enter this ion as the search ion. Enter the relative abundance of this ion (100% for base peak ions) and set the relative abundance window at ± 30%.

11.8.1.2 Alternate primary ions may be selected when interferences exist from ion abundance contribution from close eluting compounds.

11.8.2 Enter the remaining ions as secondary ions. Secondary ions are not be used to locate peaks within the search window, but are be used to support the qualitative identification of selected peaks. The number of secondary ions displayed for each compound search varies between compounds depending on the number of ions in the spectra >30% relative abundance.

11.8.3 Set the relative abundance windows for the secondary ions at ± 30%.

11.8.4 Establish the relative retention window for each compound. Because it is a relative retention window the same width window applies to all compounds on the quantitation list. The window must be established at a minimum of 0.06 relative retention time units.

11.9 Data Interpretation.

11.9.1 Executing Qualitative Searches. The target compounds shall be identified by analyst with competent knowledge in the interpretation of mass spectra by comparison of the sample mass spectrum to the mass spectrum of a standard of the suspected compound.

11.9.1.1 The search procedure will identify peaks within the search window using the primary ion only. Secondary ions and the relative retention are used to determine "the best match". If the best match contains secondary ions outside the relative abundance window, they will be flagged with a # sign.

11.9.2 Qualitative Identification. The qualitative identification of compounds determined by this method is based on retention time and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. Compounds are identified when the following criteria are met.

11.9.2.1 The intensities of the characteristic ions of a compound must maximize in the same scan or within one scan of each other.

11.9.2.2 The sample component must elute at the same relative retention time (RRT) as the daily standard. Criterion is the RRT of sample component must be within ± 0.06 RRT units of the standard.

11.9.2.3 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%).

11.9.2.3.1 If a chromatographic peak exhibits a spectrum containing an ion with relative abundance outside the relative abundance window is selected for reporting, the analyst must annotate the spectra that the compound qualified based on his/her best judgement. This circumstance will most often occur from coeluting compounds with similar ions or background matrix interferences.

11.9.3 Quantitative Analysis.

11.9.3.1 Once a target compound has been identified, its concentration (Section 13.4) will be based on the integrated area of the quantitation ion, normally the base peak (Table 6). The compound is quantitated by internal standard technique with an average response factor generated from the initial calibration curve.

11.9.3.2 If the sample produces interference for the primary ion, use a secondary ion to quantitate. This may be characterized by an excessive background signal of the same ion, which distorts the peak shape beyond a definitive integration. Also interference could severely inhibit the response of the internal standard ion. The secondary ion must be used to generate a new response factor.

11.10 Library Search for Tentatively Identified Compounds.

11.10.1 If a library search is requested, the analyst must perform a forward library search of the NIST98 mass spectral library to tentatively identify 10 to 15 non-reported compounds (15 for base, 10 for acid, 25 for base/acid fraction).

11.10.2 Guidelines for making tentative identification are listed below.

11.10.2.1 These compounds must have a response greater than 10% of the nearest internal standard. The response is obtained from the integration for peak area of the Total Ion Chromatogram (TIC).

11.10.2.2 The search is to include a spectral printout of the 3 best library matches for a particular substance. The results are to be interpreted by analyst.

11.10.2.3 Molecular ions present in the reference spectrum must be present in the sample spectrum.

11.10.2.4 Relative intensities of major ions in the reference spectrum (ions > 10 % of the most abundant ion) must be present in the sample spectrum.

11.10.2.5 The relative intensities of the major ions must agree within ± 20 %. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must between 30 and 70%).

11.10.2.6 Ions present in the sample spectrum but not in the reference spectrum must be reviewed for possible background contamination or presence of coeluting compounds.

11.10.2.7 Ions present in the reference spectrum but not in the sample spectrum must be verified by performing further manual background subtraction to eliminate the interference created by coeluting peaks and/or matrix interference.

11.10.3 Quantitation of the tentatively identified compounds is obtained from the total ion chromatogram based on a response factor of 1 and is to be tabulated on the library search summary data sheet.

11.10.4 The resulting concentration must be reported indicating: (1) that the value is estimate, and (2) which internal standard was used to determine concentration. Quantitation is performed on the nearest internal standard.

11.10.5 Peaks that are suspected to be aldol-condensation reaction products (i.e., 4-methyl-4-hydroxy-2-pentanone and 4-methyl-3-pentene-2-one) shall be searched and reported but not counted towards the total TIC count.

11.10.6 Any peak naming as “System artifact” (from the column bleedings) or “Internal Standard” (added by lab for other test, like SIM analysis) shall be searched and reported but not counted towards the total TIC count.

11.11 Selected Ion Monitoring (SIM) Option

NOTE: The use of SIM is not allowed by the SCDHEC for samples from South Carolina.

11.11.1 Instrument Set-Up: Modify the method for SIM analysis and define ion groups with retention times, ions and dwell times to include base peak ion for the target compounds of interest, surrogates, and internal standards (Table 2a, Table 8a) Select a mass dwell time of 50 milliseconds for all compounds.

11.11.2 Calibration: Calibrate the mass spectrometer in the selected ion monitoring mode using 7 calibration standards of 0.02, 0.05, 0.10, 0.20, 1.0, 2.5, 5.0 ug/ml. Spike each standard with the SIM specific internal standard solution at 4ug/ml. Calculate individual response factors and response factor RSDs using the procedures and criteria described in Section 10.1.6, 10.1.7.3 and 10.1.7.4.

11.11.3 Initial Calibration Verification. Verify the initial calibration after its completion using a 1.0 ug/ml calibration standard purchased or prepared from a second standards reference materials source. The initial calibration verification must meet the criteria of Section 10.2.2.

11.11.4 Continuing Calibration Verification. Verify the initial calibration every 12 hours using a 1.0 or 2.5 ug/ml calibration. The continuing calibration verification must meet the criteria of Section 10.3.

11.11.5 Sample Extract Analysis: Each extract has been previously spike with the SIM internal standard at 4 ug/ml. Analyze the sample extracts for the compounds of interest using the SIM scan parameters employed for the calibration standards.

11.11.6 Surrogate Standard Calculation.. Report surrogate spike accuracy for the surrogates spiked for the full scan GC/MS analysis at 50 ug/ml.

12.0 QUALITY CONTROL

12.1 QC Requirements Summary.

Daily GC/MS Performance Checks	Beginning of the analytical shift and every 12 hours
Initial Calibration	Whenever needed.
Second Source Calibration Check	Following initial calibration
Continuing Calibration Verification	Every 12 hours.
Method Blank	One per extraction batch*.
Blank Spike	One per extraction batch*.
Matrix Spike	One per extraction batch*.
Matrix Spike Duplicate	One per extraction batch*.
Surrogate	Every sample extract and standard.
Internal Standard	Every sample extract and standard.

*The maximum number of samples per batch is twenty or per project specification.

12.2 Daily GC/MS Performance Checks.

12.2.1 Refer to Section 11.2.

12.3 Initial Calibration.

12.3.1 Refer to Section 10.1.

12.4 Initial Calibration Verification (ICV) - Source Calibration Check.

12.4.1 Refer to Section 10.2.

12.5 Continuing Calibration Verification.

12.5.1 Refer to section 10.3.

12.6 Method blank.

12.6.1 The method blank is either reagent water or anhydrous sodium sulfate (depending on the sample matrix) which must be extracted with each set of 20 or less samples. For a running batch, a new method blank is required for each different extraction day. The method blank is then extracted and carried through all stages of the sample preparation and measurement.

12.6.2 If the method blank contains a target analyte above its MDL , the entire batch must be re-extracted and re-analyzed.

12.6.3 Surrogate compounds are added to the method blank prior to extraction. If the surrogate accuracy in the method blank does not meet in house criteria , it must be reanalyzed. If the reanalysis confirms the original data, the entire batch must be re-extracted.

12.7 Blank Spike

12.7.1 A blank spike must be extracted with each set of 20 or less samples. For a running batch, a new blank spike is required for each different extraction day. The blank spike consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same volume. It is spiked with the same analytes at the same concentrations as the matrix spike/matrix spike duplicate.

12.7.2 The blank spike recoveries must be assessed using laboratory in house limits.

12.7.3 If a blank spike is out of control, the following corrective actions must be taken and all the associated samples must be re-extracted and reanalyzed. The exception is if the blank spike recovery is high and no hits reported in associated samples and QC batch. In that case, the sample results can be reported with footnote (remark) and no further action is required.

12.7.3.1 Check to be sure that there are no errors in the calculations, or spike solutions. If errors are found, recalculate the data accordingly.

12.7.3.2 Check instrument performance. If an instrument performance problem is identified, correct the problem and reanalyze the sample batch.

12.7.3.3 If no problem is found, re-extract and reanalyze the sample batch.

12.8 Matrix Spike(MS) / Matrix Spike Duplicate(MSD)

12.8.1 One sample is randomly selected from each extraction batch and spiked in duplicate to assess the performance of the method as applied to a particular matrix and to provide

information on the homogeneity of the matrix. Both the MS and MSD are carried through the complete sample preparation, and determinative procedures.

12.8.2 Matrix spikes are prepared by spiking an actual sample at a concentration of 50 μg/l for both base/neutral and acids.

12.8.3 Assess the matrix spike recoveries (% R) (Section 13.5) and relative percent difference (RPD) (Section 13.6) against the in house control limits.

12.8.4 If the matrix spike accuracy of any individual compound is out of control, the accuracy for the compound in the blank spike must be within control. In such case, matrix interference is assumed and the data is reported with footnote (e.g., spike recovery indicates possible matrix interference). No further corrective action is required.

12.9 Surrogates

12.9.1 All standards, blanks, sample extracts, and matrix spikes contain surrogate compounds which are used to monitor the performance of the extraction and analytical system.

12.9.2 The recoveries (Section 13.5) of the surrogates must be evaluated to determine whether or not they fall within surrogate control limits developed by the laboratory annually.

12.9.3 If the recovery of any surrogate compound does not meet the control limits, the calculation must be checked for possible error. The surrogate solution must be checked for degradation. Contamination and instrument performance must also be reviewed.

12.9.3.1 Reanalyze the extract if no calculation errors are detected. If the surrogate recoveries for the reanalyzed extract are in control, report the data from the reanalysis only.

12.9.3.2 If the data from the reanalysis is also out of control, re-extract and reanalyze the sample.

12.9.3.3 If, upon reanalysis, the surrogate recoveries are acceptable, report the reanalysis data. If the holding time has expired prior to the reanalysis, report both the original and reanalysis results and note the holding time problem.

12.9.3.4 If the recovery is again not within limits, the problem is considered to be matrix interference. Submit both data sets with the original analysis being reported.

12.9.4 If the sample exhibits matrix interference, defined as excessive signal where target or non-target responses are greater than the response of the internal standards. In this case, reanalysis may not be required following team leader/manager approval; the surrogates will be qualified as outside the limits due to matrix interference. Alternatively, sample may be reanalyzed on dilution, if the reanalysis is again not within the limit, the sample must be reported with a footnote indicating that there were possible matrix interference.

12.10 Internal Standards.

12.10.1 Retention time for all internal standards must be within ± 30 seconds of the corresponding internal standard in the latest continuing calibration or 50 μg/ml standard of initial calibration.

12.10.2 The area (Extracted Ion Current Profile) of the internal standard in all analyses must be within 50 to 200 % of the corresponding area of the latest calibration standard (12 hr. time period).

12.10.3 If the area of internal standard does not meet control limits, the calculations must be checked. If a problem is not discovered, the sample must be reanalyzed.

12.10.4 If the areas are acceptable upon reanalysis, the reanalysis data is reported.

12.10.5 If the areas are unacceptable upon reanalysis, then both sets of data are submitted with the original analysis reported.

12.11 Refer to Project Specific Bench Notes(MS8270) for additional program or client specific QC requirements

13.0 CALCULATION

13.1 Response Factor (RF).

$$RF = \frac{A_s \times C_{is}}{A_{is} \times C_s}$$

where:

A_s = Area of the characteristic ion for the compound being measured.
A_{is} = Area of the characteristic ion for the specific internal standard.
C_s = Concentration of the compound being measured (μg/ml).
C_{is} = Concentration of the specific internal standard (μg/ml).

13.2 Percent Relative Standard Deviation (%RSD).

$$\%RSD = \frac{SD}{RF_{av}} \times 100$$

where:

SD = Standard Deviation.
RF_{av} = Average response factor from initial calibration.

13.3 Percent Difference (%D).

$$\%\ D = \frac{|\ RF_{av} - RF_{cv}\ |}{RF_{av}} \times 100$$

where: RF_{cv} = Response factor from Calibration Verification Standard.

13.4 Concentration (Conc.).

13.4.1 <u>for water:</u>

$$\text{Conc. } (\mu g/l) = \frac{A_s \times C_{is} \times V_f \times D \times 1000}{A_{is} \times RF_{av} \times V_i}$$

13.4.2 <u>for soil/sediment</u> (on a dry weight basis):

$$\text{Conc. } (\mu g/kg) = \frac{A_s \times C_{is} \times V_f \times D \times 1000}{A_{is} \times RF_{av} \times W_s \times S}$$

where:

V_f = Final Volume of total extract (ml).
D = Secondary dilution factor.
V_i = Initial volume of water extracted (ml).
W_s = Weight of sample extracted (g).
S = (100 - % moisture in sample) / 100.

13.5 Percent Recovery (%R).

$$\%\ R = \frac{\text{Concentration found}}{\text{Concentration spiked}} \times 100$$

13.6 Relative Percent Difference (RPD).

$$RPD = \frac{|MSC - MSDC|}{(1/2)(MSC+MSDC)} \times 100$$

where:

MSC = Matrix Spike Concentration.
MSDC = Matrix Spike Duplicate Concentration.

13.7 Percent Breakdown.

$$\%\ \text{Breakdown for DDT} = \frac{\text{Total DDT degradation peak area}}{\text{Total DDT peak area}} \times 100$$

where:

Total DDT degradation peak area = DDE + DDD
Total DDT peak area = DDT + DDE + DDD.

13.8 Linear regression by the internal standard technique.

$$C_s = \left(\frac{\frac{A_s}{A_{is}} - b}{a} \right) \times C_{is}$$

Where:
Cs = concentration of target analyte
As = Area of target analyte
Cis = concentration of the internal standard
b = Intercept
a = slope of the line

$$a = \frac{N \Sigma xy - \Sigma x \Sigma y}{N \Sigma x^2 - (\Sigma x)^2}$$

$$b = \frac{\Sigma y - a \Sigma x}{N}$$

N = number of points
x = amount of analyte
y = response of instrument

13.9 Correlation Coefficient

$$r = \frac{\Sigma(x - \bar{x})(y - \bar{y})}{\sqrt{\Sigma(x - \bar{x})^2 \Sigma(y - \bar{y})^2}}$$

Where r = correlation coefficient
x = amount of analyte
y = response of instrument

$\bar{x}$ = average of x values

$\bar{y}$ = average of y values

14.0 DOCUMENTATION

14.1 The Analytical Logbook is a record of the analysis sequence; the logbook must be completed daily. Each instrument will have a separate logbook.

14.1.1 If samples require reanalysis, a brief explanation of the reason must be documented in this log.

14.1.2 Overwriting of data files is never allowed.

14.2 The Standard Preparation Logbook must be completed for all standard preparations. All information requested must be completed, the page must be signed and dated by the respective person.

14.2.1 The Accutest Lot Number must be cross-referenced on the standard vial.

14.3 The Instrument Maintenance Logbook must be completed when any type of maintenance is performed on the instrument. Each instrument has a separate log.

14.4 Any corrections to laboratory data must be done using a single line through the error. The initials of the person and date of correction must appear next to the correction.

14.5 Unused blocks of any form must be X'ed and Z'ed by the analyst before submitting the data for review.

14.6 Supervisory (or peer) personnel must routinely review (at least once per month) all laboratory logbooks to ensure that information is being recorded properly. Additionally, the maintenance of the logbooks and the accuracy of the recorded information must also be verified during this review.

15.0 DATA REVIEW AND REPORTING

15.1 Initial and continuing calibration check. Verify that all calibration and continuing calibration criteria have been achieved. If the criteria had not been achieved, corrective action must be performed to bring the system in control before analyzing any samples.

15.1.1 If samples had been analyzed under non-compliant calibration criteria, all sample extracts must be re-analyzed once the system is brought into control.

15.2 Quality Control Data Review. Review all QC data. If QC criteria were not achieved, perform corrective action before proceeding with analysis.

15.2.1 In some situation, corrective action may demand that the entire sample batch be re-extracted and re-analyzed before processing data.

15.3 Chromatogram Review. The chromatogram of each sample is evaluated for target analytes.

15.3.1 Each sample may require the reporting of different target analytes. Review the login to assure that the correct target compounds are identified.

15.3.2 Manual integration of chromatographic peaks must be identified by the analysts. Upon review, the supervisor will initial and date the changes made to the report.

15.4 Transfer to LIMS. Following the initial screen review, transfer the processed data to the LIMS.

15.4.1 Compare the printed values to the original values to verify transfer accuracy.

15.4.2 If transfer errors occurred, the errors must be corrected before the data is re-submitted.

16.0 POLLUTION PREVENTION & WASTE MANAGEMENT

16.1 Users of this method must perform all procedural steps in a manner that controls the creation and/or escape of wastes or hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids or solids to the environment must be followed. All method users must be familiar with the waste management practices described in section 16.2.

16.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the waste management SOP, EHS004. This document describes the proper disposal of all waste materials generated during the testing of samples as follows:

16.2.1 Non hazardous aqueous wastes.
16.2.2 Hazardous aqueous wastes
16.2.3 Chlorinated organic solvents
16.2.4 Non-chlorinated organic solvents
16.2.5 Hazardous solid wastes
16.2.6 Non-hazardous solid wastes

Table 1 – Target Compounds by SW846 8270C			
Benzenethiol (1)	4-Bromophenyl phenyl ether	Di-n-octyl phthalate	5-Nitro-o-toluidine (1)
Benzoic Acid	Butyl benzyl phthalate	Diethyl phthalate	Naphthalene
2-Chlorophenol	Benzyl Alcohol	Dimethyl phthalate	Nitrobenzene
4-Chloro-3-methyl phenol	1,1'-Biphenyl (1)	2,3-Dichloroaniline (1)	n-Nitrosodimethylamine
2,4-Dichlorophenol	Butyl Stearate (1)	Decane	4-Nitroquinoline 1-Oxide (1)
2,4-Dimethylphenol	2-Chloronaphthalene	Octadecane (1)	N-Nitroso-di-n-propylamine
2,4-Dinitrophenol	4-Chloroaniline	bis(2-Ethylhexyl)phthalate	N-Nitrosodi-n-butylamine
2,6-Dichlorophenol	Carbazole	Ethyl methanesulfonate	N-Nitrosodiethylamine
4,6-Dinitro-2-methylphenol	Caprolactam (1)	Famphur	N-Nitrosodiphenylamine
Dinoseb	Chlorobenzilate	Fluoranthene	N-Nitrosomethylethylamine
2-Methylphenol	Chrysene	Fluorene	N-Nitrosomorpholine
3&4-Methylphenol	Cumene (1)	Hexachlorobenzene	N-Nitrosopiperidine
2-Nitrophenol	bis(2-Chloroethoxy)methane	Hexachlorobutadiene	N-Nitrosopyrrolidine
4-Nitrophenol	bis(2-Chloroethyl)ether	Hexachlorocyclopentadiene	O,O,O-Triethyl phosphorothioat
Pentachlorophenol	bis(2-Chloroisopropyl)ether	Hexachloroethane	2-Picoline
Phenol	4-Chlorophenyl phenyl ether	Hexachlorophene	Parathion
2,3,4,6-Tetrachlorophenol	1,2-Dichlorobenzene	Hexachloropropene	Pentachloroethane (1)
2,4,5-Trichlorophenol	1,2-Diphenylhydrazine	Indene (1)	Pentachlorobenzene
2,4,6-Trichlorophenol	1,3-Dichlorobenzene	Indeno(1,2,3-cd)pyrene	Pentachloronitrobenzene
2-Acetylaminofluorene	1,4-Dichlorobenzene	Isodrin	Phenacetin
4-Aminobiphenyl	2,4-Dinitrotoluene	Isophorone	Phenanthrene
Acenaphthene	2,6-Dinitrotoluene	Isosafrole	Phorate
Acenaphthylene	3,3'-Dichlorobenzidine	Kepone	Pronamide
Acetophenone	3,3'-Dimethylbenzidine	1-Methylnaphthalene	Pyrene
Aniline	1,4-Dioxane (1)	2-Methylnaphthalene	Pyridine
Anthracene	7,12-Dimethylbenz(a)anthracene	3-Methylcholanthrene	p-Phenylenediamine
Aramite	Dimethylnaphthalenes (total) (1)	4,4'-Methylenebis(2-chloroaniline)	Quinoline (1)
Atrazine (1)	Diallate	Methapyrilene	Safrole
alpha-Terpineol	Dibenz(a,h)acridine	Methyl methanesulfonate	1,2,4,5-Tetrachlorobenzene
A,A-Dimethylphenethylamine	Dibenzo(a,h)anthracene	Methyl parathion (1)	1,2,4-Trichlorobenzene
Benzidine	Dibenzofuran	6-Methyl Chrysene (1)	1,2,3-Trichlorobenzene (1)
Benzaldehyde (1)	Dimethoate	1,4-Naphthoquinone	1,3,5-Trichlorobenzene (1)

Benzo(a)anthracene	Diphenylamine	1-Naphthylamine	Thionazin (1)
Benzo(a)pyrene	Disulfoton	2-Naphthylamine	o-Toluidine
Benzo(b)fluoranthene	m-Dinitrobenzene	2-Nitroaniline	sym-Trinitrobenzene (1)
Benzo(g,h,i)perylene	p-(Dimethylamine) azobenzene (1)	3-Nitroaniline	Tetraethyl dithiopyrophosphate (1)
Benzo(k)fluoranthene	Di-n-butyl phthalate	4-Nitroaniline	

(1) NELAC Accreditation is not offered for this compound.

Table 2 – RECOMMENDED OPERATING CONDITIONS: Gas Chromatograph/ Mass Spectrometer	
Injection Type	Splitless
Carrier Gas (linear velocity)	Helium at 30 cm/sec*
Mass range	35-500 AMU
Electron Energy	70 volts (nominal)
Scan time	not to exceed 1 sec. per scan
Injection port temperature	200-300 °C
Source temperature	220-270 °C
Transfer line temperature	250-300 °C
Analyzer temperature	220-250 °C
Gas Chromatograph Temperature Program*	
Initial temperature	40-50 °C*
Time 1	2-4 minutes*
Column temperature rate	8-25 degrees/min*
Final temperature	290-320 °C according to column type*
Total run time	*20-40 minutes*

***** Parameter modification allowed for performance optimization as long as QC criteria are achieved.

Table 2a – SIM Group Parameters		
Group No.	**Retention Time (minutes)**	**Ions**
1	0 – 7.8	150, 64, 93, 82, 152, 99, 63, 128, 112, 42, 95
2	7.8 – 11	150, 128, 225, 142, 172, 152, 129, 223, 141, 171, 122, 127, 227, 115, 170
3	11 – 13.8	172, 152, 166, 182, 334, 266, 176, 153, 165, 330, 284, 264, 174, 154, 77, 332, 286, 268
4	13.8 – 18	266, 179, 202, 122, 268, 212, 203, 284, 178, 213, 244, 286
5	18 – 22	244, 229, 167, 122, 226, 202, 228, 149, 203
6	22 – 34.7	264, 149, 253, 278, 263, 150, 250, 139, 265, 252, 276, 138

Table 3 - DFTPP KEY IONS AND ION ABUNDANCE CRITERIA	
Mass	**Ion Abundance Criteria**
51	30-60 of mass 198
68	<2 % of mass 69
70	<2 % of mass 69
127	40-60 % of mass 198
197	<1 % of mass 198
198	Base peak, 100 % relative abundance
199	5-9 % of mass 198
275	10-30 % of mass 198
365	>1 % of mass 198
441	Present but less than mass 443
442	>40 % of mass 198
443	17-23 % of mass 442

Table 4 – INTERNAL STANDARDS	
Internal Standard (Full Scan)	**Prim/Sec. ions**
1,4-Dichlorobenzene-d4	152 / 150, 115
Naphthalene-d8	136 / 68
Acenaphthene-d10	164 / 162, 160
Phenanthrene-d10	188 / 94, 80
Chrysene-d12	240 / 120, 236
Perylene-d12	264 / 260, 265
Internal Standard (SIM)	**Prim/Sec. ions**
1,2-Dichlorobenzene-d4	152/ 150
1-Methylnaphthalene-d10	150/ 152, 122
Fluorene-d10	174/ 176
Fluoranthene-d10	212/ 213
Benzo(a)pyrene- d12	264/ 263, 265

Table 6 – Full Scan Semivolatile Internal Standards with Corresponding Analytes Assigned for Quantitation			
1,4-Dichlorobenzene-d4	**Ions**	**Acenaphthene-d10**	**Ions**
Aniline	(93/66,65)	Acenaphthene	(154/153,152)
Benzaldehyde	(105)	Acenaphthylene	(152/151,153)
Benzenethiol	(110)	1-Chloronaphthalene	(162/127,164)
Benzyl alcohol	(108/79,77)	2-Chloronaphthalene	(162/127,164)
Bis(2-chloroethyl)ether	(93/63,95)	4-Chlorophenylphenyl ether	(204/206,141)
Bis (2-chloroisopropyl)ether	121	Dibenzofuran	(168/139)
2-Chlorophenol	(128/64,130)	Diethyl phthalate	(149/177,150)
Cumene	(105,120)	Dimethyl phthalate	(163/149,164)
Decane	(43)	m-Dinitrobenzene	(168)
1,3-Dichlorobenzene	(146/148,111)	2,4-Dinitrophenol	(184/63,154)
1,4-Dichlorobenzene	(146/148,111)	2,4-Dinitrotoluene	(165/63,89)
1,2-Dichlorobenzene	(146/148,111)	2,6-Dinitrotoluene	(165/63,89)
1,4 Dioxane	(88)	Fluorene	(166/165,167)
Ethyl methanesulfonate	(79/109,97)	Hexachlorocyclopentadiene	(295/237,142)
2-Fluorophenol (SURR.)	(112)	1,4 – Naphthoquinone	(158)
Hexachloroethane	(117/201,199)	1- Naphthylamine	(143/115,116)
Indene	(116)	2- Naphthylamine	(143/115,116)
Methyl methanesulfonate	(80/79,64)	2-Nitroaniline	(65/92,138)
2-Methylphenol	(108/107,79)	3-Nitroaniline	(138/108,92)
4-Methylphenol	(108/107,79)	4-Nitroaniline	(138/108,92)
N-Nitrosodiethylamine	(102)	4-Nitrophenol	(139/109,65)
N-Nitrosodimethylamine	(74/42)	5 Nitro-o-toluidine	(152)
N-Nitroso-di-n-propylamine	(70/101,130)	Pentachlorobenzene	(250/252,248)
N-Nitrosomethyethylamine	(42)	Pentachloronitrobenzene	(237/235,272)
N-Nitrosomorpholine	(56)	Phenacetin	(108/109,179)
N-Nitrosoptrrolidine	(41)	Phorate	(75)
O-Toluidine	(106)	Pronamide	(173/175,145)
Petachloroethane	(167)	1,2,4,5-Tetrachlorobenzene	(216/214,218)
Phenol	(94)	2,3,4,6-Tetrachlorphenol	(232/230,131)
Phenol-d5 (SURR.)	(99)	Tetraethyldithiopyrophosphate	(322)
2-Picoline	(93/66,92)	Thioazin	(143)
Pyridine	(79)	2,4,6-Trichlorophenol	(196/198,200)
		2,4,5-Trichlorophenol	(196/198,200)

Table 6 (cont'd) – Full Scan Semivolatile Internal Standards with Corresponding Analytes Assigned for Quantitation			
Naphthalene-d8	**Ions**	**Phenanthrene-d10**	**Ions**
A,A-Dimethylphenethylamine	(58)	4-Aminobiphenyl	(169/168,170)
Acetophenone	(105/77,51)	Anthracene	(178/176,179)
Benzoic acid	(184/92,185)	Atrazine	(58)
Bis(2-chloroethoxy)methane	(93/95,123)	4-Bromophenyl phenyl ether	(248/250,141)
Caprolactam	(55)	Carbazole	(167)
4-Chloroaniline	(127)	Diallate	(86)
4-Chloro-methylphenol	(107/144)	Dimethoate	(87)
2,3 Dichloroaniline	(161)	Di-n-Butyl phthalate	(149/150)
2,4-Dichlorophenol	(162/164,98)	4,6-Dinitro-2-methylphenol	(198/51,105)
2,6-Dichlorophenol	(162/164,98)	Dinoseb	(211)
Dimethylnaphthalene	(156)	Diphenylamine	(169/168,167)
2,4-Dimethylphenol	(122/107)	1,2-Diphenylhydrazine	(77/105)
a,a-Dimethyl-phenethylamine	(58/91,42)	Disulfoton	(88)
Hexachlorobutadiene	(225/223,227)	Fluoranthene	(202/101,203)
Hexachloroprene	(213)	2-Fluorobiphenyl (SURR)	(172)
Isophorone	(82/95,138)	Hexachlorobenzene	(284/142,249)
Isosafrole	(127)	Isodrin	(193)
1-Methylnaphthalene	(142)	Methapyriline	(58)
2-Methylnaphthalene	(142/141)	Methyl Parathion	(125)
Naphthalene	(128/129,127)	N-Nitrosodiphenylamine	(169/168,167)
Nitrobenzene	(77/123,65)	4-Nitroquinoline 1-oxide	(190)
Nitrobenzene-d5 (SURR.)	(82)	Octadecane	(57)
N-Nitroso-di-n-butylamine	(84/57/41)	Parathion	(109)
2-Nitrophenol	(139/109,65)	Pentachlorophenol	(266/264,268)
Quinoline	(129)	Phenanthrene	(178/179,176)
N-Nitrosopiperidine	(42/114,55)	Pronamide	(173)
p-Phenylenediamine	(108)	sym- Trinitrobenzene	(213)
O,O,O-Triethylphosphorthioat	(198)	2,4,6 Tribromophenol (SURR)	(330)
Safrole	(162)		
alpha –Terpineol	(128)	**Perylene-d12**	**Ions**
1,2,3-Trichlorobenzene	(180/182,145)	Benzo(b)fluoranthene	(252/125)
1,2,4-Trichlorobenzene	(180/182,145)	Benzo(k)fluoranthene	(252/125)
1,3,5-Trichlorobenzene	(180/182,145)	Benzo(g.h.i)perylene	(276/138,277)
		Benzo(a)pyrene	(252/253,125)
Chrysene-d12	**Ions**	Dibenz(a,j)acridine	(279/280)
2 –Acetylaminofluorene	(181)	Dibenz(a,h)anthracene	(278/139,279)
Aramite	(194)	7,12-Dimethylbenz(a)anthracene	(256/241,257)
Benzidine	(184)	Di-n-Octyl Phthalate	(149)
Benzo(a)anthracene	(228/229/226)	Hexachlorophene	(196)
Bis(2-ethylhexyl)phthalate	(149/167,279)	Indeno(1,2,3-d)pyrene	(276)
Butylbenzyl phthalate	(149/91)	3-Methylchloanthrene	(268/253)
Chlorobenzilate	(251)		
Chrysene	(228/226,229)		
3,3'-Dichlorobenzidine	(252/254,126)		
p-Dimethylaminoazobenzene	(120/225,77)		
3,3 Dimethylbenzidine	(212)		
Famphur	(218)		
Kepone	(272)		
Methyl Chrysene	(242)		
Pyrene	(202/200,203)		

Terphenyl-d14 (SURR.)	(244)		
Table 6a – SIM Semivolatile Internal Standards with Corresponding Analytes Assigned for Quantitation			
1,4-Dichlorobenzene-d4	**Ions**	**Fluoranthene-d10**	**Ions**
2-Fluorophenol (Surr)	(112)	Fluoranthene	202, 101, 203
Phenol-d5 (Surr)	(99)	Pyrene	202, 203
Bis-(2-chloro-ethyl)ether	93, 63, 95	Terphenyl-d14 (Surr)	(244)
Nitrobenzene-d5 (Surr)	(82)	Benzo(a)anthracene	228, 229, 226
		Chrysene	228, 226, 229
1-Methylnaphthalene-d10	**Ions**	Bis(2-ethylhexylphthalate	149, 167, 279
Naphthalene	128, 129, 127		
Hexachlorobutadiene	225, 223, 227	**Benzo(a) pyrene-d12**	**Ions**
2-Methyl Naphthalene	142, 141, 115	Di-n-octyl phthalate	149, 150, 43
2-Fluorobiphenyl (Surr)	(172)	Benzo(b)fluoranthene	252, 253
		Benzo(k)fluoranthene	252, 125
Fluorene-d10	**Ions**	Benzo(a)pyrene	252, 253, 125
Acenaphthylene	152, 151, 153	Indeno(1,2,3-cd)pyrene	276, 277, 138
Acenaphthene	153, 152, 154	Dibenzo(a,h)anthracene	278, 139, 279
Fluorene	166, 165, 167	Benzo(g,h,i)perylene	276, 138, 277
1,2-Diphenylhydrazine	77, 105, 182		
2,4,6-Tribromophenol (Surr)	(330)		
Hexachlorobenzene	284, 286		
Pentachlorophenol	266, 264		
Phenanthrene	178, 179, 176		
Anthracene	178, 176, 179		

Table 7. STANDARD PREPARATION

Table 7A – Intermediate Calibration Standard Solution				
Stock Solution	**Stock Conc., µg/ml**	**Volume Added, µl**	**Final Vol. in $MeCl_2$, ml**	**Final Conc. µg/ml**
Semivolatile Standard Mix # 1	2,000	500	10	100
Semivolatile Standard Mix # 2	2,000	500	10	100
Semivolatile Standard Mix # 4	2,000	500	10	100
Semivolatile Standard Mix # 5	2,000	500	10	100
Semivolatile Standard Mix # 6	2,000	500	10	100
Semivolatile Standard Mix # 7	2,000	500	10	100
PAH Mixture #2	2,000	500	10	100
Semivolatile Standard Mix # 8	2,000	500	10	100
Additional Requested Compound(s) Mix	2,000	500	10	100
Pyridines Mixture	2,000	500	10	100
1,2,3-Trichlorobenzene	1,000	1,000	10	100
1,3,5-Trichlorobenzene	1,000	1,000	10	100
Butyl Stearate	10,000	200	10	200
Pentachlorophenol	1,000	1,000	10	100
B/N Surrogate Standard Mix	5,000	200	10	100
Acid Surrogate Standard Mix	7,500	134	10	100.5

Table 7B – Intermediate Calibration Standard Solution -SIM				
Stock Solution	**Stock Conc., µg/ml**	**Volume Added, µl**	**Final Vol. in $MeCl_2$, ml**	**Final Conc. µg/ml**
Semivolatile Standard Mix # 1	2,000	50	10	10
Semivolatile Standard Mix # 2	2,000	50	10	10
Toxic #2	2,000	50	10	10
PAH Mixture #2	2,000	50	10	10
Semivolatile Standard Mix # 8 (Acids)	2,000	250	10	50
1-Methynaphthalene	1,000	100	10	10
B/N Surrogate Standard Mix	5,000	100	10	50
Acid Surrogate Standard Mix (Full Scan)	7500	67	10	50

Table 7C – Initial Calibration Standards Prep Scheme

Standard Solution	**Intermediate Conc., µg/ml**	**Intermediate added, µl Full Scan**	**Final Volume in $MeCl_2$, ml**	**Final Conc., µg/ml – Full Scan**
STD 1	100	1,000	1	100
STD 2	100	800	1	80
STD 3	100	500	1	50
STD 4	100	250	1	25
STD 5	100/10 (SIM)	100	1	10
STD 6	100	50	1	5
STD 7	100	20	1	2
STD8	100	10	1	1

Table 7D Initial Preparation Standards Prep Scheme - SIM				
Standard Solution	**Intermediate Conc., µg/ml**	**Intermediate added, µl SIM**	**Final Volume in $MeCl_2$, ml**	**Final Conc., µg/ml – SIM Scan**
STD 1	10/50	500	1	5 BN / 25 Acids
STD 2	10/50	250	1	2.5 BN / 12.5 Ac
STD 3	10/50	100	1	1 BN / 5 Acids
STD 4	1	200	1	0.2 BN / 1 Acids
STD 5	1	100	1	0.1 BN / 0.5 Acids
STD7	0.1	500	1	0.05 BN / 0.25 AC
STD 6	0.1	200	1	0.02 BN / 0.1 AC

Table 7E– ICV -Second Source Calibration Check Standard				
Intermediate	**Intermediate Conc., µg/ml**	**Volume Used, µl (Full/SIM)**	**Final Volume in Acetone, ml**	**Final Conc., µg/ml (Full/SIM)**
Base Neutrals Mixture	100	500/ 50	1	50/ 5
Acid Mixture	100	500/ 50	1	50/ 5

Table 8a –Selected Ion Monitoring: Masses and Dwell Times		
Compound	**Mass Ion (m/z)**	**Dwell Time (ms)**
Acenaphthene	153, 152, 154	50
Acenaphthylene	152, 151, 153	50
Anthracene	178, 176, 179	50
Benzo(a)anthracene	228, 229, 226	50
Benzo(a)pyrene	252, 253, 125	50
Benzo(b)fluoranthene	252, 253	50
Benzo(g,h,i)perylene	276, 138, 277	50
Benzo(k)fluoranthene	252, 125	50
Chrysene	228, 226, 229	50
Dibenzo(a,h)anthracene	278, 139, 279	50
Fluoranthene	202, 101, 203	50
Fluorene	166, 165, 167	50
Indeno(1,2,3-cd)pyrene	276, 277, 138	50
Naphthalene	128, 129, 127	50
Phenanthrene	178, 179, 176	50
Pyrene	202, 203	50
2-Methyl Naphthalene	142, 141, 115	50
Bis-(2-chloro-ethyl)ether	93, 63, 95	50
Pentachlorophenol	266, 264	50
Hexachlorobutadiene	225, 223, 227	50
1,2-Diphenylhydrazine	77, 105, 182	50
Bis(2-ethylhexylphthalate	149, 167, 279	50
Di-n-octyl phthalate	149, 150, 43	50
Hexachlorobenzene	284, 286	50
2-Fluorophenol	112, 64, 63	50
Phenol-d5	99, 42	50
Nitrobenzene-d5	82, 128	50
2-Fluorobiphenyl	172, 171, 170	50
2,4,6-Tribromophenol	330, 332, 334	50
Terphenyl-d14	244, 122	50

Table 9. REPORTING LIMITS

Compound	Water	Soil	Compound	Water	Soil
	µg/l	µg/kg		µg/l	µg/kg
Benzoic Acid	20	667	Chlorobenzilate	5	167
2-Chlorophenol	5	167	Chrysene	1	33
4-Chloro-3-methylphenol	5	167	bis(2-Chloroethoxy)methane	2	67
2,4-Dichlorophenol	5	167	bis(2-Chloroethyl)ether	2	67
2,4-Dimethlyphenol	5	167	Bis(2-Chloroisopropyl)ether	2	67
2,4-Dinitrophenol	20	667	4-Chlorophenyl phenyl ether	2	67
4,6-Dinitro-o-cresol	20	667	1,2-Dichlorobenzene	2	67
Dinoseb	5	167	1,3-Dichlorobenzene	2	67
2-Methylphenol	2	67	1,4-Dichlorobenzene	2	67
4-Methylphenol	2	67	2,4-Dinitrotoluene	2	67
2-Nitrophenol	5	167	2,6-Dinitrotoluene	2	67
4-Nitrophenol	10	333	3,3'-Dichlorobenzidine	5	167
Pentachlorophenol	10	333	3,3’-Dimethylbenzidine	5	167
Phenol	2	67	7,12-Dimethylbenz(a)anthracene	5	167
2,3,4,6-Tetrachlorophenol	5	167	Diallate	5	167
2,4,5-Trichlorophenol	5	167	Dibenzo(a,h)anthracene	1	33
2,4,6-Trichlorophenol	5	167	Dibenzofuran	2	67
2-Acetylaminofluorene	5	167	Dimethoate	5	167
4-Aminobiphenyl	5	167	Diphenylamine	5	167
Acenaphthene	1	33	Disulfuton	5	167
Acenaphthylene	1	33	m-Dinitrobenzene	5	167
Acetophenone	5	167	p-(Dimethylamine)azobenzene	5	167
Aniline	2	67	Di-n-butyl phthalate	2	67
Anthracene	1	33	Di-n-octyl phthalate	2	67
Aramite	5	167	Diethyl phthalate	2	67
A,A-Dimethylphenethylamine	5	167	Dimethyl phthalate	2	67
Benzo(a)anthracene	1	33	bis(2-Ethylhexyl)phthalate	2	67
Benzo(a)pyrene	1	33	Ethyl methansulfonate	5	167
Benzo(b)fluoranthene	1	33	Famphur	30	1000
Benzo(g,h,i)perylene	1	33	Fluoranthene	1	33
Benzo (k)fluoranthene	1	33	Fluorene	1	33
4-Bromophenyl phenyl ether	2	67	Hexachlorobenzene	2	67
Butyl benzyl phthalate	2	67	Hexachlorobutadiene	1	33
Benzyl Alcohol	2	67	Hexachlorocyclopentadiene	20	667
2-Chloronaphthalene	2	67	Hexachloroethane	5	167
4-Chloroaniline	5	167	Hexachlorophene	50	1700
Carbazole	1	67	Hexachloropropene	5	167

Table 9 (Cont'd)

Compound	Water	Soil	Compound	Water	Soil
	µg/l	µg/kg		µg/l	µg/kg
Indeno(1,2,3-cd)pyrene	1	33	N-Nitrosomethylethylamine	5	167
Isodrin	5	167	N-Nitrosomorpholine	5	167
Isophorone	2	67	N-Nitrosopiperidine	5	167
Isosafrole	5	167	N-Nitrosopyrrolidine	5	167
Kepone	30	1000	O,O,O Triethylphosphorothioat	5	167
2-Methylnaphthalene	2	667	2-Picoline	5	167
3-Methylcholanthene	5	167	Parathion	5	167
Methapyrilene	5	167	Pentachlorobenzene	5	167
Methyl Methanesulfonate	5	167	Pentachloroethane	5	167
Methyl Parathion	5	167	Pentachloronitrobenzene	5	167
1,4 Naphthoquinone	5	167	Phenacetin	5	167
1-Naphthylamine	5	167	Phenanthrene	1	33
2-Naphthylamine	5	167	Phorate	5	167
2-Nitroaniline	5	167	Pronamide	5	167
3-Nitroaniline	5	167	Pyrene	1	33
4-Nitroaniline	5	167	Pyridine	2	67
5-Nitro-o-toluidine	5	167	p-Phenylenediamine	5	167
Naphthalene	1	33	Safrole	5	167
Nitrobenzene	2	67	1,2,4,5 Tetrachlorobenzene	5	167
n-Nitrosodimethylamine	2	67	1,2,4-Trichlorobenzene	2	67
4-Nitroquinoline-1-Oxide	10	333	Thionazin	5	167
N-Nitroso-di-n-propylamine	2	67	o-Toluidine	5	167
N-Nitrosodi-n-butylamine	5	167	sym-Trinitrobenzene	5	167
N-Nitrosodiethylamine	5	167	Tetraethyl dithiopyrophosphate	5	167
N-Nitrosodiphenylamine	5	167			

Table 10. Selected Ion Monitoring Reporting Limits

Compound	Water	Soil	Compound	Water	Soil
	µg/l	µg/kg		µg/l	µg/kg
Pentachlorophenol	0.3	17	Fluoranthene	0.1	3.3
Acenaphthene	0.1	3.3	Fluorene	0.1	3.3
Acenaphthylene	0.1	3.3	Hexachlorobenzene	0.02	3.3
Anthracene	0.1	3.3	Hexachlorobutadiene	0.1	3.3
Benzo(a)anthracene	0.1	3.3	Indeno(1,2,3-cd)pyrene	0.1	3.3
Benzo(a)pyrene	0.1	3.3	2-Methylnaphthalene	0.1	3.3
Benzo(b)fluoranthene	0.1	3.3	Naphthalene	0.1	3.3
Benzo(g,h,i)perylene	0.1	3.3	Phenanthrene	0.1	3.3
Benzo (k)fluoranthene	0.1	3.3	Pyrene	0.1	3.3
Chrysene	0.1	3.3	bis(2-Chloroethyl)ether	0.2	6.6
Dibenzo(a,h)anthracene	0.1	3.3	Bis (2-ethylhexyl) phthalate	0.2	6.6
1,2-Diphenylhydrazine	0.2	6.6	Di-n-octyl phthalate	0.2	6.6